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A COMPARISON OF THE QUINHYDRONE AND HYDROGEN ELECTRODES IN SOLUTIONS CONTAINING TANNIN

E. L. Wallace and John Beek, jr.

ABSTRACT

Measurements of pH are made with the hydrogen and quinhydrone electrodes in solutions of tanning extracts and in systems consisting of leather and water in equilibrium. Comparison of the values obtained with the two electrodes indicates that the quinhydrone electrode can not be substituted for the hydrogen electrode in solutions of the types studied. However, a satisfactory correction could be applied for the leathers studied, a necessary condition being that the nature of the solution be exactly known. In the case of tanning extracts, the errors involved were too great to be disregarded.

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I. INTRODUCTION

In laboratories which handle a large quantity of analytical or control work in connection with the leather industry, a method for pH determination which is rapid and simple is highly desirable. The quinhydrone electrode developed by E. Biilmann [1] provides such a method; and, when its use became general, there was a tendency in leather laboratories to accept the results obtained with this electrode as equivalent to hydrogen electrode values.

Several investigators [2] have noted discrepancies between measurements made with the quinhydrone and the hydrogen electrode. Quite recently, Pleass [3] has reported on An Investigation of the Methods Employed for the Determination of the pH Value of Tan Liquors and Lime Liquors.

Pleass found that a colorometric method gives fairly good results if used with proper precautions; that the glass electrode gives correct results for all conditions investigated; that the results obtained with the hydrogen electrode are correct if the density of the liquor is less than 60° Bk. and the liquor is free from substances leading to an oxidation-reduction potential, such as sulphites and sulphides; that

[1] Ann. Chim., **15**, p. 109; and **16**, p. 321; 1921.
[2] Atkin and Thompson, J. S. L. T. C., **8**, p. 183; 1924. De La Bruere, J. S. L. T. C., **9**, p. 438; 1925. J. A. Wilson, The Chemistry of Leather Manufacture, 2d ed., **1**, p. 108.
[3] J. Soc. Chem. Ind., **48**, p. 152 T; 1929.

"the quinhydrone electrode was unreliable for all the trade tan liquors examined."

In view of the general use of the quinhydrone electrode, it seemed worth while to investigate the possibility of finding a correction factor to be used in interpreting results to be obtained with this method. It is to be noted that Pleass's examination was confined to "trade tan liquors," which were presumably indefinite blends of different kinds of tanning materials. In our work, each type of material has been investigated separately, in solutions of known composition, with the thought that if a correction factor for each type could be found, it might be possible to explain the discrepancies noted when blended liquors are examined.

II. PURPOSE

In connection with other work under way at this bureau it is necessary to make hundreds of measurements of the pH values of leather. For this purpose it was desired to use the quinhydrone electrode because of its greater speed. A comparison has, therefore, been made of the quinhydrone and the hydrogen electrodes when used to measure the pH values of leather as well as the pH values of tanning liquors.

III. APPARATUS AND MATERIALS

The apparatus used in this work was designed for the rapid handling of a large number of routine samples rather than for accurate measurement. (Fig. 1.) However, the accuracy of the apparatus is better than the reproducibility of electrometric measurements in the solutions in question. Six solution bridges (*A*) furnished with stopcocks are arranged radially about a central well (*B*) of saturated KCl solution, which in turn is connected through a bridge (*C*) of the same solution and another well (*D*) to the reference half-cell (*E*). The reference half-cell is a saturated KCl calomel electrode. A saturated KCl solution was used for electrical contact with the solutions investigated,[4] in order to eliminate as nearly as possible any error due to contact potential. Dropping funnels (*F*) are inserted in the top of the central well and in the electrode cell so that the system may be flushed out to prevent contamination. In the case of the solutions of tanning extract a bridge consisting of an agar gel saturated with KCl was inserted between the extract and KCl solutions.

The hydrogen electrodes (*G*) used were of the Hildebrand type, the electrodes being of platinum, plated with electrolytically deposited palladium black. The hydrogen was supplied direct through a manifold from a tank (*H*) of the commercial product.

Gold wires about 0.6 mm in diameter, sealed in glass tubes with about 1 cm projecting, were used for the quinhydrone electrodes. The quinhydrone was prepared in this laboratory by the method of Biilmann and Lund.[5]

The apparatus was checked frequently with *N*/20 potassium acid phthalate solution, and was always found to be correct within the experimental error of the work.

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[4] Loomis, N. E., and Acree, S. F., Am. Chem. J., **46**, p. 621; 1911

[5] Ann. Chim., **16**, p. 321.

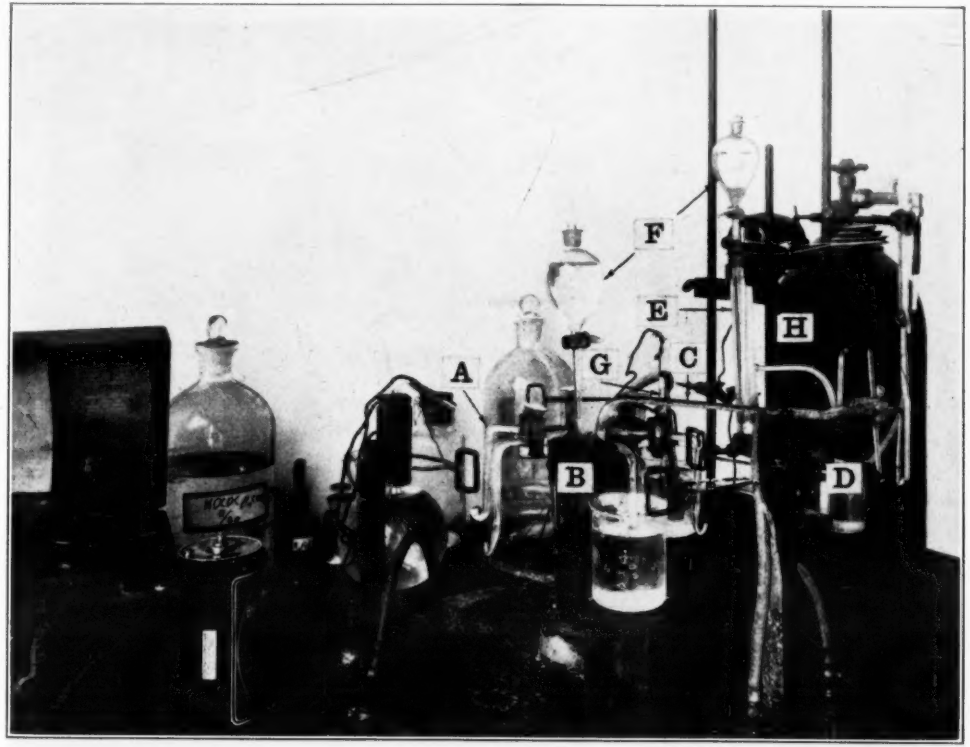

FIGURE 1.—*Assembly of apparatus used for making pH measurements*

The solutions of tanning materials were made from the commercial solid extracts.

In investigating the pH values of leather, steer-hide leathers tanned with the following types of tanning materials were used: (1) Powdered chestnut extract, (2) solid ordinary quebracho extract, (3) solid sulphited quebracho extract, and (4) a blend consisting of about 3 parts chestnut extract and 1 part quebracho extract. The first three were tanned at the Bureau of Standards, while the fourth was a commercial leather.

The sulphuric acid was added to the leather samples by immersing them in solutions of concentrations varying from one-half to 8 per cent H_2SO_4.

Each sample was analyzed for moisture by the official method of the American Leather Chemists Association, and for total sulphur by oxidizing a sample with nitric acid and then determining total sulphate gravimetrically by the barium sulphate method. The difference between the percentage thus determined and that found in the untreated leather of the same type was calculated as H_2SO_4 and taken as the percentage of H_2SO_4 in the sample.

IV. EXPERIMENTAL METHOD

The tanning extracts were taken from stock solutions, the tannin content of which was determined by the official method of the American Leather Chemist's Association.

The pH values of the leather were measured in accordance with the method of Kohn and Crede.[6] This consists of weighing 4.9 g of dry leather into a beaker, adding 100 ml distilled water, and allowing two hours for the system to come to equilibrium before making a reading.

A small quantity (0.1 g) of $K_3Fe(CN)_6$ was added to the solutions before making the hydrogen electrode measurements to prevent poisoning of the electrodes by copper, which was present in small amounts, being derived, presumably, from the copper linings of extract evaporators. The presence of ferricyanide ion lowered the concentration of copper ion sufficiently to prevent displacement of copper from solution by the hydrogen. No measurable error was found to be introduced by the addition of the $K_3Fe(CN)_6$. The measurements with both electrodes were made on the same solution, an excess of solid quinhydrone being added after the hydrogen e. m. f. was determined. The readings with the quinhydrone electrode were not taken until they became fairly constant.

Check determinations were made on duplicate samples to determine whether the quantity of hydrogen dissolved by the solution in equilibrium with the gas at atmospheric pressure would have a measurable effect on the reading with the saturated quinhydrone electrode. No effect was observed.

The following is an outline giving the nature of the solutions studied:

1. Extract solutions, over a range of tannin concentrations: (*a*) Chestnut extract, (*b*) quebracho extract, (*c*) equal parts chestnut and quebracho extract.

[6] J. Am. Leather Chem. Assoc., 18 p. 189; 1923.

2. Leather-water equilibrium systems, over a range of weight of leather per 100 ml water: (*a*) Leather tanned with chestnut extract, containing (1) zero per cent H_2SO_4 and (2) 4½ per cent H_2SO_4; (*b*) leather tanned with sulphited quebracho extract, containing (1) zero per cent H_2SO_4, (2) 2 per cent H_2SO_4, and (3) 4 per cent H_2SO_4.

3. Leather-water equilibrium systems over a range of acid content in the leather: (*a*) Leather tanned with powdered chestnut extract, (*b*) leather tanned with solid ordinary quebracho extract, (*c*) leather tanned with solid sulphited quebracho extract, and (*d*) leather tanned with commercial blend.

A number of determinations were made on filtered solutions from leather-water equilibrium systems. These solutions gave substantially the same results as when the leather was present, so no further work was done on them.

In order to determine approximately the probable error of a single reading for each of the electrodes, e. m. f. measurements were made for 10 duplicate samples of commercial leather. The probable error of a single observation with the hydrogen electrode was found to be about 0.5 mv, and that with the quinhydrone electrode about 1.0 mv. Converted into pH, these quantities become 0.008 and 0.017. In view of the magnitude of these errors the e. m. f. readings were not taken more closely than to the nearest millivolt.

While the work was all done at room temperature and barometric pressure, the calculations are based on a temperature of 25° and a pressure of 760 mm. The errors introduced by variation in temperature and pressure were neglected, as they were not large in comparison with other experimental errors.

The e. m. f. measurements with the hydrogen and quinhydrone electrodes were calculated to corresponding pH values, pH_H and pH_Q, respectively, and these are given as curves showing pH plotted against the independent variable. (Figs. 2 to 10.) Where the difference between the pH values given by the two electrodes is plotted as $pH_Q—pH_H$, or Δ pH, the scale for Δ pH is on the right-hand side of the graph.

V. DISCUSSION OF RESULTS

In none of the systems studied are the results obtained with the hydrogen and quinhydrone electrodes in close agreement. At particular points the two electrodes give the same values, but the results obtained with quinhydrone could not, in general, be substituted without correction for those obtained with hydrogen.

Because of the wide variation in the types of curves showing the quinhydrone correction, no attempt has been made to formulate a general expression for this correction.

No quantitative explanation of the discrepancies observed in any case studied can be offered at present, but several possible causes of errors in the quinhydrone electrode e. m. f. readings may be given.

The ratio of the activities of quinone and quinol in a solution in equilibrium with an excess of solid quinhydrone is changed in the three following ways, (1) by reduction or oxidation of quinhydrone,[7] (2) by a difference in the effect of dissolved substances on the two

[7] G. Hugonin, Cuir. Tech., **13**, p. 385; 1924; J. S. L. T. C., **8**, pp. 492 and 537; 1924; J. Am. Leather Chem. Assoc., **20**, p. 52; 1925.

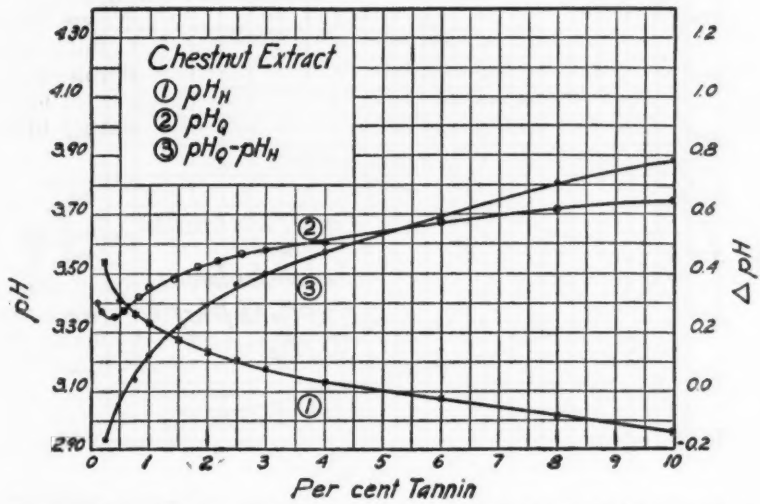

FIGURE 2.—*pH measurements in solutions of powdered chestnut wood extract, over a range of tannin concentration*

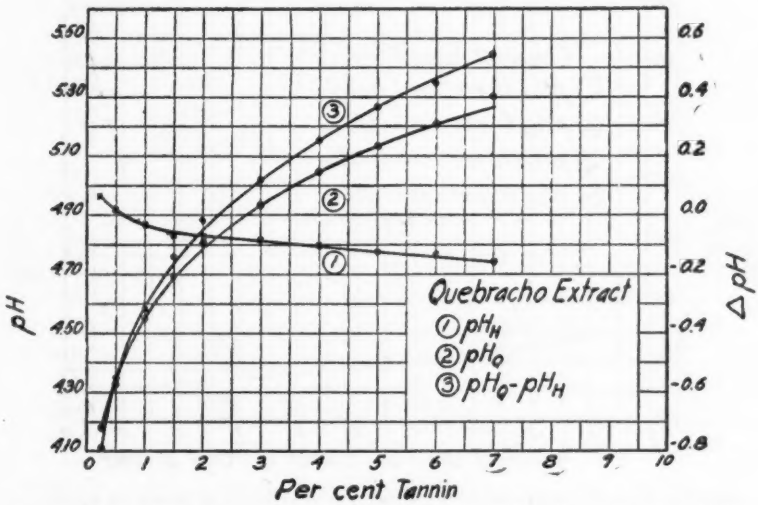

FIGURE 3.—*pH measurements in solutions of solid ordinary quebracho extract, over a range of tannin concentration*

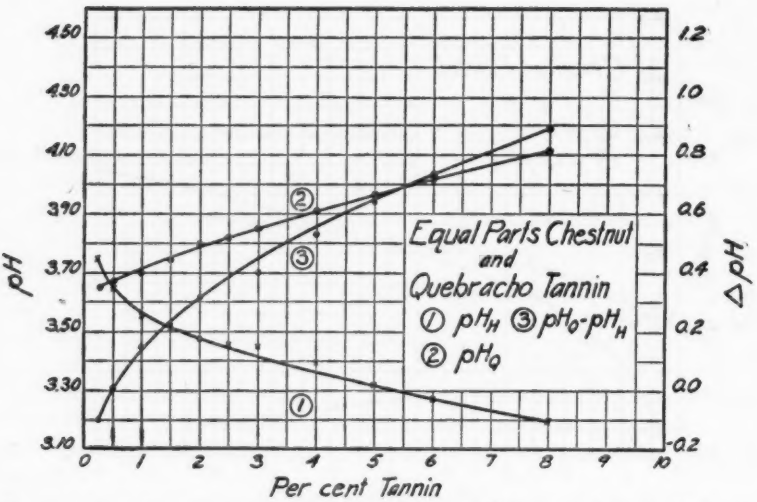

FIGURE 4.—*pH measurements in solutions containing equal parts of chestnut and quebracho tannins, over a range of tannin concentration*

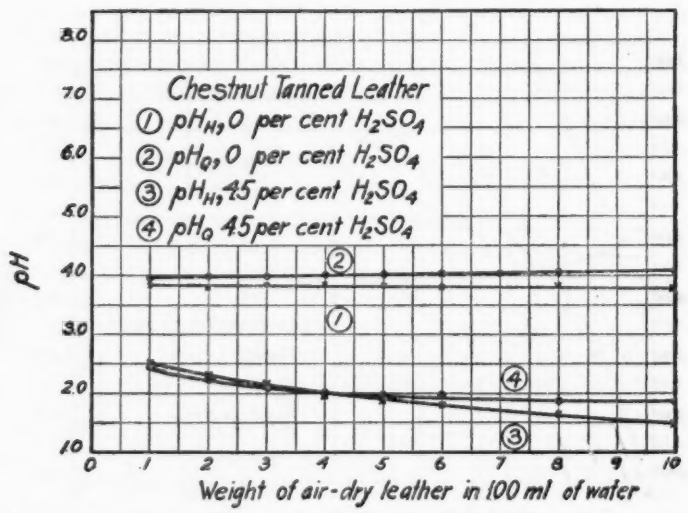

FIGURE 5.—*pH measurements in systems consisting of water in equilibrium with leather tanned with chestnut extract, over a range of weight of leather per 100 ml water*

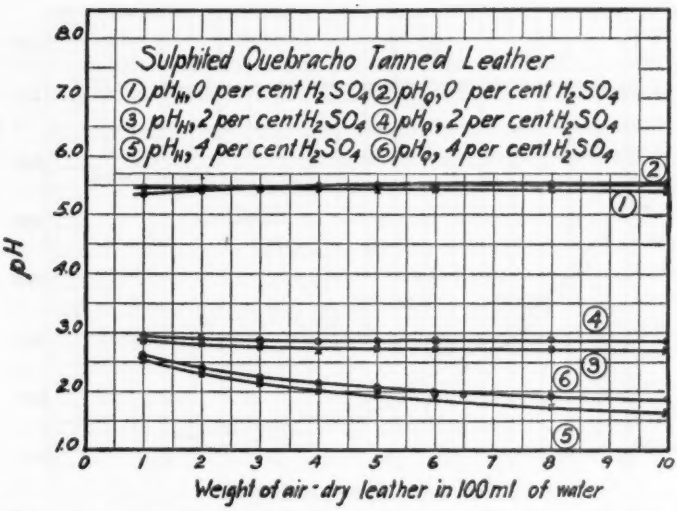
Sulphited Quebracho Tanned Leather
① pH_H, 0 per cent H_2SO_4 ② pH_Q, 0 per cent H_2SO_4
③ pH_H, 2 per cent H_2SO_4 ④ pH_Q, 2 per cent H_2SO_4
⑤ pH_H, 4 per cent H_2SO_4 ⑥ pH_Q, 4 per cent H_2SO_4
pH
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0 1 2 3 4 5 6 7 8 9 10
Weight of air-dry leather in 100 ml of water

FIGURE 6.—*pH measurements in systems consisting of water in equilibrium with leather tanned with sulphited quebracho extract, over a range of weight of leather per 100 ml water*

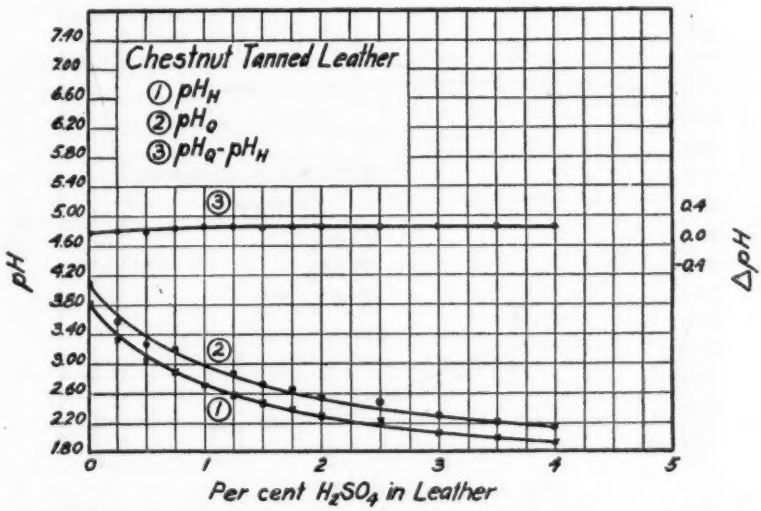

FIGURE 7.—*pH measurements in systems consisting of water in equilibrium with leather tanned with chestnut extract, over a range of sulphuric acid content in the leather*

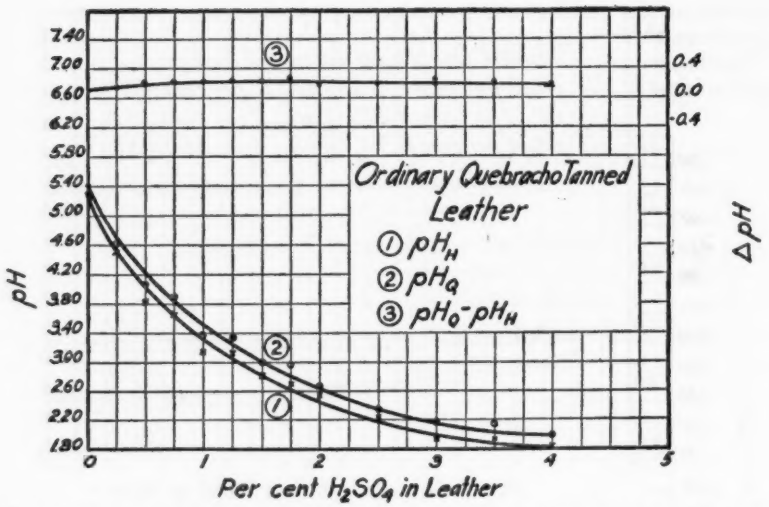

FIGURE 8.—*pH measurements in systems consisting of water in equilibrium with leather tanned with ordinary quebracho extract over a range of sulphuric acid content in the leather*

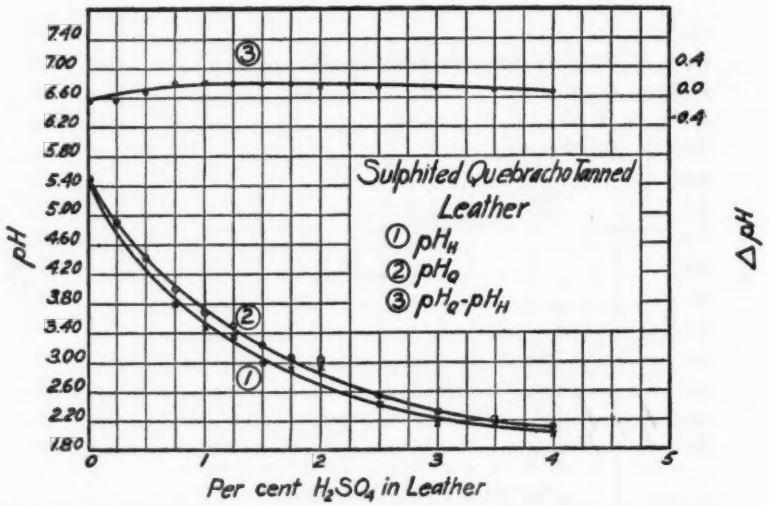

FIGURE 9.—*pH measurements in systems consisting of water in equilibrium with leather tanned with sulphited quebracho extract over a range of sulphuric acid content in the leather*

activities,[8] and (3) by a difference in the quantity of the two compounds adsorbed on the surface of colloidal matter.

In view of the fact that leather and tanning materials contain polyphenolic and other related substances the first effect is probably most important in the cases under consideration.

The experimental results indicate that quinhydrone electrode readings for the pH of leather water systems can be corrected to corre-

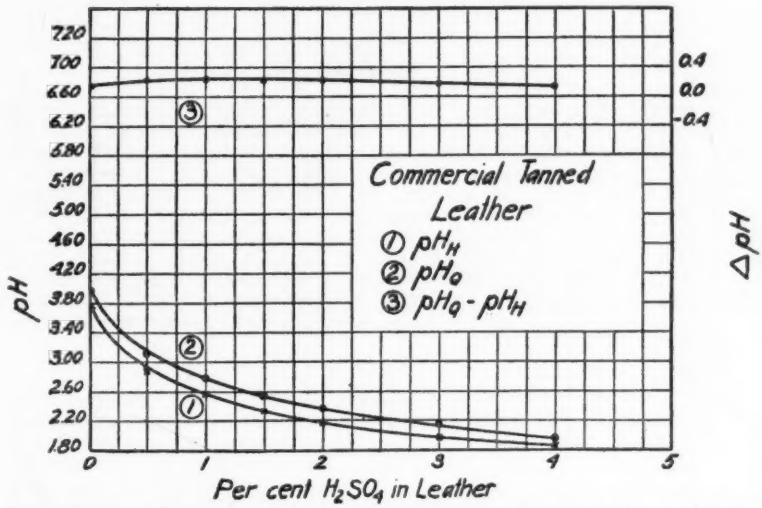

FIGURE 10.—*pH measurements in systems consisting of water in equilibrium with leather tanned with a commercial blend, over a range of sulphuric acid content in the leather*

spond with hydrogen electrode readings in case the exact nature of the solutions in question is known. Such corrections have been used successfully in this laboratory. In the case of tanning extracts the errors involved are too great to be disregarded.

WASHINGTON, December 19, 1929.

[8] E. Billmann, Bull. Soc. Chim., **41**, p. 213; 1927.

A GAS ANALYSIS PIPETTE FOR DIFFICULT ABSORPTIONS

By Martin Shepherd

ABSTRACT

This note describes a bubbling pipette which employs a thin platinum distributor plate perforated with 200 holes of 0.06 mm diameter. This distributor plate breaks the influent gas stream into many small bubbles, and effects intimate contact between a liquid reagent and the gas to be absorbed. The efficiency of the pipette has been compared with the ordinary bubbling type and with the Dennis-Friedrichs pipette. Oxygen is completely removed from air during three passages into alkaline pyrogallol contained in both the new pipette and the Dennis–Friedrichs pipette, whereas 10 passages were required for the ordinary type. The new pipette possesses some advantages over the Dennis-Friedrichs design, mainly lower cost, simplicity of construction, less fragility, and the fact that no special molds are required for its construction.

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IV.	Comparison of the distributor and Dennis-Friedrichs pipette	751

I. DEVELOPMENT OF THE PIPETTE

A number of gas analysis pipettes have been designed to bring the gas and reagent into intimate contact. Pipettes of the bubbling type possess distinct advantages in this respect. The ordinary bubbling pipette which appears at present in various modifications and under various names was first designed by Hankus in 1899.[1] The best modifications of this pipette so far described are one adapted from the Friedrichs gas washing bottle by L. M. Dennis [2] (fig. 1 (*b*)) and one designed by Nowicki [3] and improved by Heinz.[4] Dennis reports the complete removal of oxygen from air after three passages into alkaline pyrogallol contained in the Dennis-Friedrichs and Nowicki-Heinz pipettes.

When the Jena glass sintered filters were developed, the author constructed a pipette in which the gas inlet tube of an ordinary bubbling pipette was bent upward and tipped with a coarse Jena sintered filter. The gas stream was thus finely divided, and fairly rapid absorption resulted; but the filter plate trapped a measurable amount of gas.

Development of the idea was continued by using a platinum plate perforated with numerous small holes. It was found that when the

[1] Hankus, E. E., Osterr. Chem. Ztg., **47,** p. 81; 1899; J. Gasbel., **49,** p. 367; 1906.
[2] Dennis, L. M., Gas Analysis, p. 81 (fig. 47), The Macmillan Co., New York; 1913.
[3] Nowicki, Österr. Z. Berg. Hüttenw., **53,** p. 337; 1905.
[4] Heinz, J. Gasbel., **49,** p. 367; 1906.

plate was placed so that the burrs resulting from punching these holes were on the efflux side and the grease film ordinarily present on the platinum surface was removed, the gas stream then issued from the plate in a series of fine bubbles. With ordinary technic,

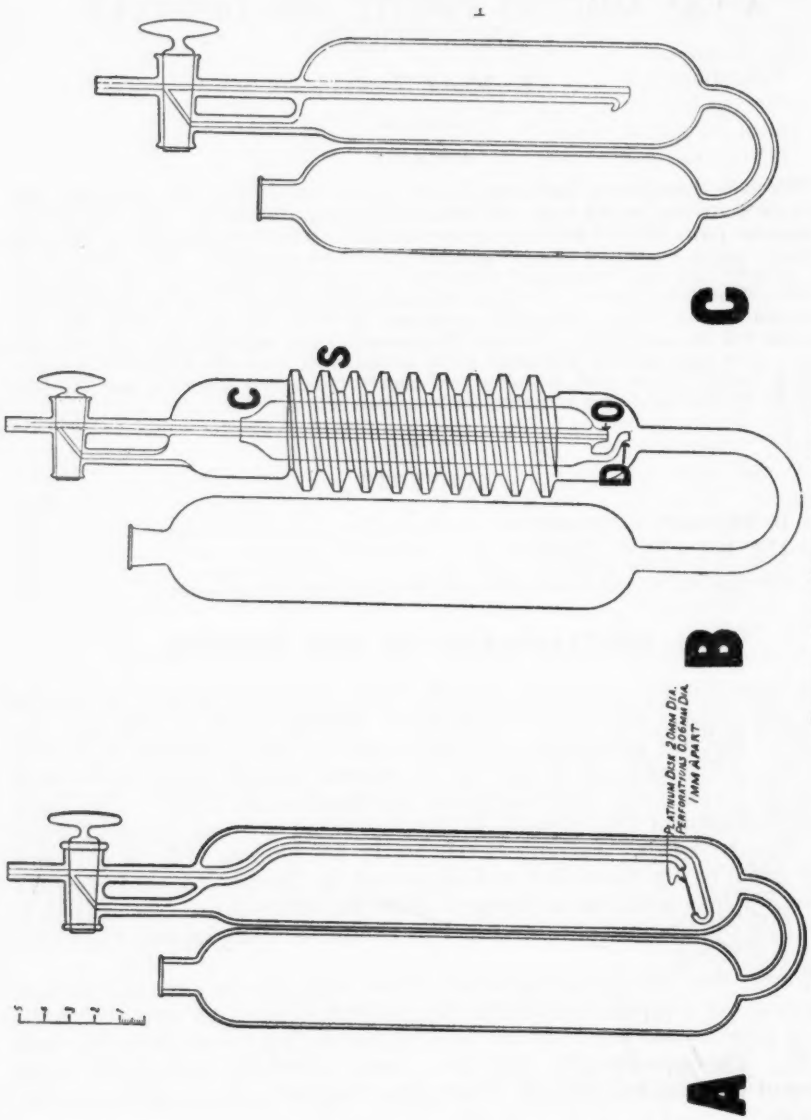

FIGURE 1.—*Absorption pipettes*

however, it was not possible to obtain holes of sufficiently uniform diameter. Accordingly the perforated plates were obtained from a company engaged in manufacturing spinnerets for the rayon industry. These proved to be entirely satisfactory.

II. DESCRIPTION OF THE PIPETTE

The pipette constructed with this gas distributing tip is shown in Figure 1 (*a*). The perforated plate is 0.05 mm thick and 20 mm in diameter. The holes are 0.06 mm in diameter ± 0.003 mm, spaced 1 mm apart, and extend within 2 mm of the outer edge of the plate. There are 212 evenly spaced holes in such a plate. The burrs resulting from drilling were not removed. The plate is sealed into the flat dish-shaped end of the gas inlet tube which is placed at an angle in order to prevent trapping the return gas.

About 30 mm mercury pressure is required to force the gas through the perforated plate. When in use the leveling bulb attached to the burette is placed slightly above the upper stopcock of the burette, and the lower burette stopcock opened to permit free passage of mercury from the leveling bulb. Under these conditions, a 100 ml sample passes into the pipette in about 20 seconds. The gas issues from the perforated plate in very small bubbles which apparently do not coalesce. A froth consisting of many very small bubbles separated by liquid films is formed on the surface of the reagent. This layer of froth is about 2 cm deep, when an alkaline pyrogallol solution is used, and some absorption must take place here as well as in the actual passage through the reagent. The froth disappears immediately when the gas flow through the perforated plate has ceased.

At the beginning of an absorption, the gas passes through approximately 7½ inches of reagent. This depth of liquid decreases to about 2½ inches for a 100 ml sample. In the Dennis-Friedrichs pipette, the effective depth of reagent is approximately 50 inches, decreasing only 2 inches with the passage of a 100 ml sample. In spite of this fact the absorption in the distributing pipette is slightly more rapid.

When a viscous reagent is used, the liquid returns slowly through the small orifices of the distributor plate and, if the ordinary technic is used, some time is lost in displacing the gas in the inlet capillary when it is desired to return the sample to the burette for final measurement. This difficulty is overcome by allowing the stopcock of the pipette to remain adjusted in the position for delivery of gas into the distributing plate and reducing the pressure in the burette about 2 cm. The reagent then flows through the perforated plate and into the capillary within a few seconds, but rises in the capillary at a very easily controlled rate. The pipette stopcock is then turned to the normal position for displacement of the gas sample, which may be returned to the burette within the same time that is required for the plain bubbling type of pipette.

III. EFFICIENCY OF THE PIPETTE

The efficiency of the pipette was determined by the absorption of oxygen from air, and of oxygen from a mixture of oxygen and nitrogen containing about 95 per cent of oxygen. The reagent used was an alkaline pyrogallol solution recommended by Anderson.[5] The absorption of oxygen by alkaline pyrogallol is somewhat slower than by other reagents which have been recommended, but for this reason it is suitable for a study of relative efficiencies. Dennis[6] also used

[5] Anderson, R. P., Ind. Eng. Chem., **7**, p. 588; 1915.
[6] Dennis, L. M., Gas Analysis, p. 82. The Macmillan Co., New York; 1913.

alkaline pyrogallol in comparing the efficiencies of several pipettes, and his results will be given for the sake of comparison.

The assembly diagram of the gas analysis apparatus used is shown in Figure 2. The burette B, manometer M, and pipette P are connected to the train T so that pressure may be balanced simultaneously in burette and train, and gas contained over the arm of the manometer connected to the train may be completely displaced into the train and burette before each passage of a sample to the pipette. A very small dead capillary space results.

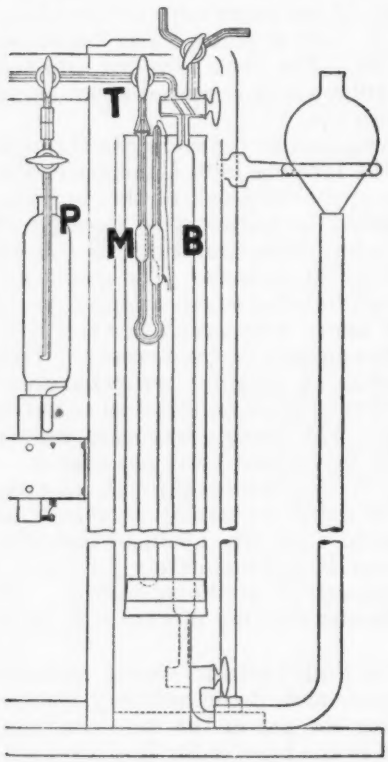

FIGURE 2.—*Assembly of apparatus*

It is not possible to pass a 100 ml sample into the Dennis-Friedrichs pipette within the 20 seconds required for complete passage into the distributor pipette. If the passage is made in less than 45 seconds, the gas collecting at the bottom of the Friedrichs spiral may be forced into the reservoir arm of the pipette and so lost. Dennis compared his pipette with others employing 1-minute passages into each pipette. The present tests were made at various rates, but some of the data are directly comparable in this respect. The data for the removal of oxygen from air are given in Table 1, and those for the removal of oxygen from 95 per cent O_2 in N_2 are given in Table 2.

TABLE 1.—*Percentage of the total oxygen content of air which is removed during each passage into various types of bubbling pipettes containing alkaline pyrogallol*

Number of passages	Type of pipette						
	Plain bubbling (fig. 1 (c))	Dennis-Friedrichs (fig. 1 (b))	Distributor (fig. 1 (a))		United States Steel Co.[1][2]	Dennis-Friedrichs [1]	Nowicki-Heinz [1]
	Time consumed for each passage						
	20 seconds	45 seconds	20 seconds	45 seconds	60 seconds	60 seconds	60 seconds
1	40.2	93.6	94.9	97.1	43.1	89.0	98.6
2	63.8	99.4	99.8	100.0	68.0	92.7	99.5
3	76.8	100.0	100.0		82.3	100.0	100.0
4	86.5				90.0		
5	91.8				94.8		
6	94.8				97.7		
7	97.2				98.6		
8	98.6				100.0		
9	99.6						
10	100.0						

[1] Results obtained by L. M. Dennis, Gas Analysis, p. 82. The Macmillan Co., New York; 1913.
[2] A plain bubbling pipette of slightly greater length than the one shown in fig. 1 (c).

TABLE 2.—*Percentage of the total oxygen content of a 95 per cent O_2+5 per cent N_2 mixture which is removed during each passage into the distributor and Dennis-Friedrich's pipettes*

Number of passages	Type of pipette		
	Distributor		Dennis-Friedrichs
	Duration of each passage		
	20 seconds	45 seconds	45 seconds
1	70.5	89.6	89.4
2	92.9	99.0	98.6
3	99.2	100.0	99.6
4	100.0	----------	99.9
5	----------	----------	100.0

The tabulated data show the following significant facts:

1. Oxygen is removed from air more quickly in the distributor pipette than in the Dennis-Friedrichs pipette. This is true for both the 20 and 45 second rates of passage. Three passages are required to complete the removal of oxygen at the 20-second rate, and two passages at the 45-second rate. The Dennis-Friedrichs pipette requires three passages at the 45-second rate. Ten passages are required in the plain bubbling type pipette (fig. 1 (*c*)) at the 20-second rate.

2. In the case of the 95 per cent oxygen sample, the distributor pipette required four passages at the 20-second rate and three passages at the 45-second rate. The Dennis-Friedrichs pipette required five passages at the slower rate. A small volume of gas remained after the second passage (about 5 ml) and the efficiency of the Dennis pipette was considerably lowered thereafter.

IV. COMPARISON OF THE DISTRIBUTOR AND DENNIS-FRIEDRICHS PIPETTES

While the distributor pipette has been shown to be more rapid, a comparison of the two pipettes should include other considerations. These may be briefly stated.

1. The outer spiral shell (*S* of fig. 1 (*b*)) of the Dennis-Friedrichs pipette is blown in a mold. The inner surface is then ground to fit the inside cylinder *C*, which terminates in a liquid inlet, *D*, and a gas outlet, *O*. The capillary tube through which the gas passes into the pipette requires two ring seals, one at the dome of the pipette and one at the bottom of the inner cylinder. This construction results in the following disadvantages:

(*a*) The construction is more complicated and expensive than that of the distributor pipette.

(*b*) The mold blown spiral is apt to be fragile. A number have been found broken in shipment. The outer shells were of uneven thickness, and some were extremely thin in places.

(*c*) In constructing the pipette, the stopcock and the capillary gas inlet must be sealed to the dome, which is drawn out from the mold

blown shell. Proper annealing is then evidently difficult, since a number of pipettes have cracked at this point during normal use.

(*d*) The liquid inlet *D* of the cylinder *C* is ordinarily made with an inside diameter that varies by several millimeters. The inside diameter of this tube is somewhat critical, since it should offer slightly more resistance to the return of liquid than the spiral itself. If this is not the case, the gas bubbles which form in the flat spiral are difficult to displace when a viscous reagent—for example, alkaline pyrogallol—is used. One of the Dennis pipettes trapped gas which could not be displaced from the spiral, and others required watching.

(*e*) When gas is first introduced into the pipette it accumulates at the bottom of the spiral until some has passed through the spiral itself and displaced the reagent from the dome of the pipette. Care must be used to prevent loss of a portion of the sample into the side reservoir. This limits the speed of passage of a sample into the pipette. It has already been pointed out that 45 to 60 seconds are required for a 100 ml sample, while the same volume can be passed into the distributor pipette in 20 seconds. Furthermore, when a small residual volume is passed into the Dennis pipette, care must be taken to avoid trapping bubbles of the gas in the capillary gas outlet *O*, which will result in the formation of slugs of the reagents in this capillary when the gas is displaced into the burette.

(*f*) Molds for the construction of the Dennis pipette are not available in this country, and the pipette must be imported at present.

2. The fine orifices of the distributor plate of the new pipette may possibly become clogged by precipitation from some reagents. This difficulty has not been experienced with Anderson's solution.

WASHINGTON, January 4, 1930.

NOTE ON THE THEORY OF HEAT CONDUCTION

By M. S. Van Dusen

ABSTRACT

A simple transformation of the general equation for heat flow is given, which does not appear to be generally known. By means of this transformation most problems in steady heat flow with conductivity depending on temperature can be derived directly from the solutions of the same problems where the conductivity is assumed constant. The paper is entirely mathematical.

The general equation of heat flow by conduction is

$$\text{div}\ (k\nabla\theta) = c\frac{\partial\theta}{\partial t} \tag{1}$$

where θ is the temperature at any point at the time t, and k and c are, respectively, the thermal conductivity and the heat capacity per unit volume of the medium at the temperature θ and at the point in question.

If k is assumed to be independent of temperature, then for an isotropic medium. equation (1) reduces to the ordinary form, viz:

$$\frac{k}{c}\nabla^2\theta = \frac{\partial\theta}{\partial t} \tag{2}$$

The various treatises dealing wholly or in part with the mathematical theory of heat conduction invariably assume that both k and c are independent of temperature, and imply that otherwise the mathematical difficulties become very great. Carslaw [1] states that in some mathematical investigations the conductivity, k, is assumed to be a linear function of temperature, but does not give specific references.

It will be shown, however, that in the majority of instances the variation of k with temperature offers less difficulty than the variation of c with temperature. If the conductivity k is a known function of temperature, given by

$$k = f\ (\theta) \tag{3}$$

and if we introduce a new variable, u, defined as

$$u \equiv \int_{\theta_0}^{\theta} f\ (\beta)\ d\beta \tag{4}$$

then, by using the relations:

$$\nabla u = k\nabla\theta$$

and

$$\frac{\partial u}{\partial t} = k\frac{\partial\theta}{\partial t}$$

[1] Fourier's Series and Integrals, MacMillan & Co., p. 193; 1906.

derived from (4), the general equation (1) reduces to

$$\frac{k}{c}\nabla^2 u = \frac{\partial u}{\partial t} \tag{5}$$

∇u is the (negative) heat flux, and in equation (4) the lower limit of the integral is arbitrary. It might be conveniently taken as zero, for then when $\theta = 0$, $u = 0$.

If in equation (5) the quantity $\frac{k}{c}$, termed the diffusivity, or the thermometric conductivity, is independent of temperature, equation (5) is identical in form with equation (2). This quantity, however, is not, in general, constant; but it may be remarked that for non-crystalline poorly conducting solids the diffusivity is more nearly independent of temperature than either k or c individually, which is assumed in the classical solutions of problems in heat flow. For such materials, therefore, equation (5) with $\frac{k}{c}$ constant is a better approximation than the classical form equation (2). At any rate the physical properties of the medium in question have been combined into one variable coefficient without loss of generality.

In all problems of steady heat flow, however, the time rates of change of both θ and u vanish, the diffusivity consequently disappears, and equation (5) becomes

$$\nabla^2 u = 0 \tag{6}$$

which is identical in form with the classical equation for steady heat flow. It follows, therefore, that if the boundary conditions are expressed in terms of u instead of θ, by means of equation (4), problems of steady heat flow with variable conductivity can be attacked by the same general methods that are used in the solution of problems with constant conductivity. In fact, in all cases where the boundary conditions are originally given in terms of temperature, normal heat flux, or a combination of both, solutions for variable conductivity are immediately derivable from the solutions of the same problems with constant conductivity. The general nature of this principle has apparently been overlooked, or at least not generally recognized.

If the boundary conditions are given in terms of differential equations, as in the case of heat transfer between a boundary surface and a fluid medium according to some experimental law of heat transfer, such as Newton's law, the solutions for u do not follow directly from the solutions for θ, for then the differential equations in terms of u become different in form from those in terms of θ. For example, it may be possible to find a solution of the equation: $\nabla^2\theta = 0$, satisfying certain boundary conditions, among which is included:

$$k\frac{\partial \theta}{\partial n} + h\theta = 0 \tag{10}$$

over some portion of the boundary.

In terms of u, we must satisfy

$$\nabla^2 u = 0 \text{ in the solid}$$

and

$$\frac{\partial u}{\partial n} + hF(u) = 0 \tag{11}$$

over the same portion of the boundary, the function $F(u)=\theta$ being derived from equation (4).

It is evident that equations (11) and (10) are different in form, and the solution in u can not be derived directly from the solution in θ.

As an example of the use of equation (6), let us consider the solution of a problem which was useful in connection with the design of apparatus for measuring the thermal conductivity of metals.

One end ($z=0$) of a cylinder of length c and radius a is maintained at zero temperature, the other end ($z=c$) being insulated. Heat is added at a constant rate to a portion of the convex surface of length b adjacent to the end $z=c$, the rest of the convex surface being insulated. Required: The temperature distribution in the cylinder when the steady state has been attained.

CASE I.—*Constant thermal conductivity*

We have to solve: $\nabla^2\theta=0$, or in cylindrical coordinates:

$$\frac{\partial^2\theta}{\partial r^2}+\frac{1}{r}\frac{\partial\theta}{\partial r}+\frac{\partial^2\theta}{\partial z^2}=0 \tag{7}$$

subject to the boundary conditions:
When

$$z=0,\ \theta=0$$

$$z=c,\ \frac{\partial\theta}{\partial z}=0$$

$$\left.\begin{matrix} r=a \\ 0<z<c-b \end{matrix}\right\},\ \frac{\partial\theta}{\partial r}=0$$

$$\left.\begin{matrix} r=a \\ c-b<z<c \end{matrix}\right\},\ \frac{\partial\theta}{\partial r}=\frac{h}{k}$$

where h is the inward heat flux per unit area normal to the convex surface, and k the thermal conductivity of the material.

By considering the image of the cylinder extending from the end $z=c$ to $z=2c$, maintaining the imaginary end at zero temperature, and adding heat to the portion of the convex surface extending from $z=c$ to $z=b+c$, it is evident from symmetry that no heat will flow across the surface $z=c$, and conditions in the actual cylinder will be unchanged. By this device the solution is readily built up from known particular solutions of equation (7), and the final result is as follows:

$$\theta=\frac{8hc}{k\pi^2}\sum_{n=1}^{n\to\infty}\frac{\sin\frac{n\pi}{2}\sin\frac{n\pi b}{2c}}{-i\,n^2J_1\left(i\frac{n\pi a}{2c}\right)}\sin\frac{n\pi z}{2c}J_0\left(i\frac{n\pi r}{2c}\right) \tag{8}$$

where i is the usual symbol for $\sqrt{-1}$, and J_0 and J_1 are, respectively, Bessel's functions of orders 0 and 1.

CASE II.—*Variable thermal conductivity*

Let $k = k_0(1+\alpha\theta)$; therefore $u = k_0\left(\theta + \frac{\alpha}{2}\theta^2\right)$. We have to solve:

$$\nabla^2 u = 0$$

the boundary conditions in u being:
When

$$z = 0, \quad u = 0$$

$$z = c, \quad \frac{\partial u}{\partial z} = 0$$

$$\left.\begin{matrix} r = a \\ 0 < z < c - b \end{matrix}\right\}, \quad \frac{\partial u}{\partial r} = 0$$

$$\left.\begin{matrix} r = a \\ c - b < z < c \end{matrix}\right\}, \quad \frac{\partial u}{\partial r} = h$$

The solution for u is evidently the same as equation (8) except that θ is replaced by u, and $\frac{h}{k}$ by h alone. Substituting for u its value in terms of θ, we have finally

$$\theta + \frac{\alpha}{2}\theta^2 = \frac{8hc}{k_0\pi^2} \sum_{n=1}^{n\to\infty} \frac{\sin\frac{n\pi}{2}\sin\frac{n\pi b}{2c}}{-i\,n^2 J_1\left(i\frac{n\pi a}{2c}\right)} \sin\frac{n\pi z}{2c} J_0\left(i\frac{n\pi r}{2c}\right) \tag{9}$$

This equation can, of course, be solved explicitly for θ, or numerical calculations can be made by successive approximations, since the value of the cofficient α is ordinarily rather small. Evidently, if $\alpha = 0$, equation (9) must reduce to equation (8), for then the conductivity is constant and equal to k_0.

WASHINGTON, February 5, 1930.

BLISTERING PHENOMENA IN THE ENAMELING OF CAST IRON

By A. I. Krynitsky and W. N. Harrison

ABSTRACT

In the application of vitreous enamel to cast iron, "blisters" may form in the enamel. The Bureau of Standards, in response to a request from the American Ceramic Society, undertook a study of this phenomenon and obtained data from which the following conclusions were drawn.

Physical defects in the castings, especially "sponginess," will cause blisters, as will also faulty composition or application of enamels. There are, however, differences in the tendencies of different sound castings to give blisters when enameled under identical conditions. The gases forming these blisters are CO and CO_2.

A gray iron casting acquires in freezing and cooling a very thin surface skin, or "microchill," of varying thickness and hardness. The data indicate that removal of this skin from sound castings eliminates blistering. During the enameling process the combined carbon of this skin tends to break down to a nascent, readily oxidizable form of carbon, which evolves CO and CO_2. There are probably two kinds of nonblistering iron, one in which little combined carbon is present at the surface, and another in which it is stabilized. Some irons are more prone to give the "microchilled" layer than others. During the early stages of enameling both blistering and nonblistering irons evolve gas, which is attributed to quick oxidation of submicroscopic graphite and which escapes before the enamel has fused to a retentive condition. Addition of graphitizing agents, such as silicon, may be beneficial, but it is harder to prevent the formation of the microchill than the ordinary, or macrochill. Removal of the surface layer by deep sandblasting or "burning out" appears to be the most practical remedy for blistering of sound castings.

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I. INTRODUCTION

1. GENERAL DISCUSSION

(a) BLISTERING A TROUBLE IN ENAMELING

In the application of vitreous enamel to cast iron, as in the manufacture of household ranges, bathtubs, etc., "blisters" may form in the enamel. Blistered enamel ware is rough, unsightly, and often unserviceable.

The research committee of the enamel division of the American Ceramic Society brought the problem of blisters to the attention of the Bureau of Standards in 1924. It was stated that some cast irons were more prone to this defect than others and the problem was, therefore, studied from both the metallurgical and the ceramic points of view.

(b) ENAMELING PROCESSES

The enameling process may be carried out in several ways, depending on the type of enamel used. In the so-called dry process a suspension of enamel is sprayed or painted on a cold casting and dried, after which the coated casting is heated until this first or "ground" coat is matured. A dry second or "cover" coat is then sifted onto the hot ground coat and the piece at once reheated to mature the cover coat.

The wet process is similar to the dry process in the application of a ground coat, but the piece is then cooled and the cover coat applied in the same way as the ground coat. This is the process with which the present investigation is primarily concerned, because it is believed to furnish a better criterion of blistering tendencies than the dry process. In the two-coat processes the ground coat is more infusible than the cover coat and in firing a higher temperature is used.

In the so-called "single-coat" (wet) process the same enamel is used in the first coat as in any subsequent coat or coats, but the first coat receives a somewhat more severe firing treatment. Such single-coat enamels are usually more fusible than the two-coat wet-process enamels, often being high in lead oxide in order to produce this fusibility. The firing is done at much lower temperatures than in the other processes.

(c) BLISTERS AND GAS EVOLUTION

It is obvious that blisters are caused by gas entrapped in the enamel. Craters are evidence of the previous presence of blisters, the enamel not closing completely after the escape of the gas. Slight "dimples" will result when the enamel closes, but does not become quite level; if the enamel does become level obviously no harm is done through the previous existence of the bubble. Hence, it is not gas evolution in itself that is to be feared, but gas evolution at the wrong time. The more fluid and fusible the enamel the less likely it is to entrap bubbles or to leave a crater after a bubble breaks.

(d) VARIATIONS IN USUAL ENAMELING PRACTICE THAT AFFECT BLISTERING

The firing is a rather delicately balanced operation which is affected by changes in the rate at which heat is taken up by the load (as with loads of different weight or different weight-area ratio) or in the rate at which heat is supplied to the furnace. By manipulation of operating conditions, experienced operators can often successfully enamel irons which show some tendency to blister.

Whatever the source of the gas responsible for blisters in enamel coats, if it is evolved before the enamel starts to fuse, it is not retained in the enamel. If it is evolved while the enamel is semifluid and very viscous (under fired), it may be retained. If evolved when the enamel is fluid, it may do no harm unless it is evolved so slowly that it is not released before the enameled article is removed from the furnace. It is quite possible that a "nonblistering" iron might give off more gas, but give it off more readily and more nearly at one temperature, than a "blistering" iron.

2. IDEAS ON BLISTERING EXPRESSED BY ENAMELERS

Various facts or opinions in regard to the occurrence of and causes for blisters have been expressed by enamelers though not all of the comments were available at the beginning of the work. These are as follows:

Northern pig iron is said to produce castings which show a greater tendency to the blistering phenomenon than castings from southern pig iron, even though the castings may have closely similar chemical composition. Not all northern irons give trouble from blisters, and Malinovsky (1)[1] cites a case of blistering of southern iron. The

[1] The figures given in parentheses here and throughout the text relate to the reference numbers in the selected bibliography given at the end of this paper.

outstanding difference between northern and southern pig irons as classes is the higher phosphorus content and consequent greater fluidity of the southern iron.

Remelting of northern pig, or the admixture of 30 to 50 per cent of southern pig iron, scrap, or remelted northern pig iron with 50 to 70 per cent of virgin northern pig iron is said to reduce the tendency toward blistering. This allegation has not been definitely proved.

A British visitor stated that similar troubles met in British practice were avoided by ceasing to use pig iron from certain blast furnaces. Another British comment (2) elaborates this by stating that pig iron from slow-driven blast furnaces is considered to give fewer enameling defects, including blisters, than that from rapidly driven furnaces.

Pig iron with high manganese content is said to cause blisters. Excessively high sulphur content is also asserted to cause blisters and pinholes (2).

White iron castings for malleableizing are said to cause blisters unless properly "annealed." Gray cast-iron plates chilled on one side only are said to show a greater tendency to blistering on the chilled side. On the other hand, Staley (3, p. 140) states that it was once believed that white iron was the only kind suitable for enameling and cites Vogel as advocating a white chilled layer on gray iron for enameling purposes. Staley states that low-silicon iron, low in graphite, gives less trouble from blisters than does high-silicon iron and ascribes the effect of graphite to its reaction with metallic oxides of the enamel with the formation of carbon monoxide or dioxide gas. He states that the higher the phosphorus content of the iron the lower the silicon can be; hence, indirectly, high phosphorus tends to prevent blisters. Malinovsky (1), on the other hand, alleges that low combined carbon—that is, high graphitic carbon—favors freedom from blisters and high combined carbon produces the opposite result. He states that if temper carbon is present, blistering is certain.

The use of charcoal, sea coal, plumbago, or other carbonaceous facings on a sand mold in which a casting is made that is to be enameled is said to be detrimental. Staley (3, p. 134) advises complete avoidance of all facings. On the other hand, one enameler (while preferring to avoid charcoal facings) advocates the use of plumbago facings and pouring the metal rather cold, with the object of preventing the burning on of a layer of molding sand which may be difficult to remove by sand-blasting.

A casting which has blistered on the first attempt to enamel it, if cleaned from enamel by sand-blasting, may ordinarily be reenameled without further trouble from blistering. Heating the castings to redness (so-called "annealing" or "burning out") before sand-blasting is the generally accepted preventive of blistering. In some cases, blistering was said to be prevented by coating the sand-blasted surface with sodium dichromate solution, with the idea of increasing the oxidation of the surface, heating to redness and sand-blasting again. Danielson and Reinecker (4) made heating at 815° C. (1,500° F.) prior to sand-blasting the regular practice in their study of the properties of enamels for cast iron.

Thorough cleaning of cast iron by sand-blasting before enameling has been recognized as desirable, to avoid blistering (5, 7).

It has been stated that dry-process enamels can usually be applied without blistering to irons that will blister with a wet-process enamel.

Enamels of improper composition may be blistering of themselves; for example, a ground coat containing over 10 per cent Na_2O caused blistering (4, p. 719).

An enamel which is free from blisters when applied in proper amount may blister when too heavy a coat is applied irrespective of the composition of the metal to which it is applied (6). In a 2-coat process, if the cover coat is too high-melting in comparison with the ground coat, blisters will result (4, p. 719). It is stated (4, p. 734) that white single-coat enamels containing more than 3 to 4 per cent SnO_2 applied on cast iron, even after "burning out," caused blistering. This is ascribed to reduction of SnO_2 by graphite.

Contamination of enamel with sulphur, sulphates, greases, or other organic matter, anything that gives volatile products on heating, may cause blisters (3).

II. PRELIMINARY SERIES

1. COOPERATIVE WORK AND PRELIMINARY EXPERIMENTS

At the outset of the experimental work, it was planned that specimens representing such metallurgical variations as it was wished to study were to be made at the bureau and distributed to cooperating enamelers who would, without divulging the composition of the enamels used, enamel and return the specimens with a description of the process employed.

Northern pig irons, designated as R_1 and L_1, were supplied by the committee for these tests, which were especially designed to determine whether remelting was beneficial, as had been claimed. Iron R_1 proved to have only a slight blistering tendency while iron L_1 was strongly blistering.

Both cupola and electric furnace melting were tried. The cupola was a small experimental unit, lined to 16½ inches inside diameter. The tuyères were 17 inches from the bottom. The coke used contained 89.65 per cent fixed carbon, 9.25 per cent ash, 1 per cent volatile, 0.10 per cent moisture, 0.89 per cent sulphur, 0.016 per cent phosphorus, and had 49 per cent cell space. A representative charge was as follows: 170 pounds coke on the bed, then 100 pounds iron, 40 pounds coke, 100 pounds iron, 40 pounds coke, 100 pounds iron. To each layer of iron was added 2½ pounds oyster shells as flux. In such a heat, the first iron appeared in 8 minutes after starting the blast, the first tap being made in 18 minutes, and the last in 40 minutes. The blast entered at 4-ounce pressure and the volume of air used varied between 380 and 440 cubic feet per minute until the last 10 minutes when it rose to 500 to 540. Optical pyrometer readings of the stream of molten iron at tapping, corrected for deviation from black body radiation, gave 1,310° C. (2,390° F.) at the first tap and 1,380° C. (2,520° F.) on succeeding taps.

The electric furnace was a magnesite lined, indirect arc, rocking type furnace holding about 300 pounds of iron. It was operated at 80 to 105 volts, 1,100 to 1,400 amperes (momentary readings). The average power input was 75 kw. In a representative heat of 325 pounds iron, charged into a cold furnace, the metal was melted after 140 kw. h. had been used. Rocking of the furnace was then started. After 2½ hours with a total input of 190 kw. h., the metal was at 1,480° C. (2,700° F.). Unlike the small cupola, the electric furnace

could be made to deliver the metal at any desired temperature, and was much more satisfactory to use on an experimental scale.

The change in composition on repeated cupola melting and the much smaller change on electric melting are shown in Table 1.

It will be noted that, in cupola melting under the test conditions, the total carbon, the manganese, and the silicon decreased as a result of oxidation, whereas the sulphur increased on account of sulphur "pick up" from the coke.

In the electric furnace the total carbon, the silicon, and especially the manganese, changed very little, and there was no pick up of sulphur. When close control of the composition for experimental purposes was necessary, it was therefore much easier to use the electric furnace than the cupola.

The form of the castings used in the first part of this investigation is shown in Figure 1.

Plates from the heats given in Table 1 (except heat 21) and from several other heats to which additions of arsenic, tin, and sulphur (added as iron sulphide) had been made, were enameled either at the bureau alone, or with different enamels at the bureau and cooperating plants, and examined for blisters.

TABLE 1.—*Change in composition of pig iron on repeated meltings in cupola and electric furnace*

Iron	Furnace and melt	Heat No.	Carbon			Mn	P	S	Si
			Total	Graphitic	Combined				
			Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
R_1	Original pig		3.62	3.06	0.55	0.78	0.83	0.029	2.99
R_1	Cupola, first	7	3.40	3.18	.22	.69	.81	.048	2.82
R_1	Cupola, second	12	3.25	2.84	.41	.57	.84	.058	2.77
R_1	Cupola, third	13	3.22	2.74	.48	.44	.84	.086	2.69
R_1	Electric, first	9	3.62	3.05	.57	.73	.80	.026	2.90
R_1	do	23	3.66	3.17	.49	.73	.80	.023	2.77
R_1	Electric, second	11	3.76	3.28	.48	.71	.79	.030	2.85
L_1	Original pig		3.81	3.15	.66	.67	.46	.045	2.31
L_1	Cupola, first	6	3.65	2.97	.68	.56	.46	.050	2.16
L_1	do	14	3.47	3.07	.40	.57	.46	.076	2.24
L_1	Cupola, second	15	3.51	2.74	.77	.42	.46	.083	2.07
L_1	Cupola, third	16	3.47	2.95	.52	.33	.47	.095	1.92
L_1	Cupola, fourth	21	3.34	1.89	1.45	.24	.46	.108	1.70
L_1	Cupola, fifth	25	3.20	.99	2.21	.18	.47	.125	1.51
L_1	Electric, first	8	3.67	3.16	.51	.62	.47	.048	2.32
L_1	do	17	3.76	3.10	.66	.63	.47	.038	2.19
L_1	Electric, second	10	3.97	3.34	.63	.62	.44	.017	2.19

With dry-process enamel, all specimens enameled at the bureau behaved excellently except for a few large blisters on heat 25, iron L_1, which as a result of remelting (five times in the cupola) had very high combined carbon and low silicon. One firm, using a dry-process enamel, reported satisfactory results on various heats of both R_1 and L_1 except heat 25. Another firm, using dry-process enamel, also reported good results with R_1 and some specimens of L_1 whether from cupola or electric furnace in the case of first melts in which the sulphur had been raised to 0.10 to 0.12 per cent. They reported poor results, however, with the electric furnace melts not having sulphur additions and with the L_1 cupola remelts.

With wet-process enamels, one cooperating firm used no ground coat, but instead two coats of a very low melting white enamel. They reported severe blistering on all specimens of both irons. However, by merely increasing the firing time on the second coat from 12 to 17 minutes, a great improvement resulted on the few repeat tests that were made, some specimens being practically perfect.

At the bureau, specimens coated with ground coat Rg–1, fired at 900° C. (1,650° F.) and followed by a white cover coat, R–14, blistered badly. The compositions of ground and cover coats are given in Tables 2 and 3.

TABLE 2.—*Composition of ground coat Rg–1* [1]

COMPOSITION OF MELTED FRIT

Ground coat No.	Flint	B_2O_3	Na_2O	PbO
	Per cent	*Per cent*	*Per cent*	*Per cent*
Rg-1	69.90	13.57	8.53	8.00

COMPOSITION OF BATCH; 100 PARTS OF MELTED FRIT

Ground coat No.	Flint	Borax	Sodium nitrate	Red lead
	Per cent	*Per cent*	*Per cent*	*Per cent*
Rg-1	69.90	36.96	6.95	8.17

[1] Ground coat Rg-1, B. S. Tech. Paper No. 246, pp. 702, 703 (used with 15 per cent clay).

TABLE 3.—*Composition of white cover enamels R–11 and R–14* [1]

COMPOSITION OF MELTED FRIT

Enamel No.	Feldspar	Flint	B_2O_3	Na_2O	PbO	ZnO	CaF_2	Cryolite
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
R–11	33.0	12.0	9.0	8.5	21.0	6.0	5.5	5.0
R–14	38.0	12.0	4.0	8.5	21.0	6.0	5.5	5.0

COMPOSITION OF BATCH; 100 PARTS OF MELTED FRIT

Enamel No.	Feldspar	Flint	Borax	Sodium nitrate	Soda ash	Red lead	Zinc oxide	Fluorspar	Cryolite
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
R–11	33.0	12.0	24.52	6.20	3.86	21.60	6.0	5.5	5.0
R–14	38.0	12.0	10.90	6.20	7.70	21.60	6.0	5.5	5.0

[1] White cover enamels R-11 and R-14, B. S. Tech. Paper No. 246, pp. 708–709.

One firm enameled some specimens with wet-process enamel, the ground coat being fired at 870° C. (1,600° F.) for eight minutes, the cover coat at 840° C. (1,545° F.) for seven minutes (composition of enamels not given). The results of these tests are shown in Table 4, together with similar ones carried out at the bureau, rated on a scale in which 100 represents a perfect piece with no blisters and 0 a piece with an average of one or more blisters per square inch (18 blisters on the 18 square inch specimen).

One might conclude that iron R_1 is, on the whole, not a "blistering" iron, whereas L_1 is a strongly "blistering" iron. From the results of the bureau tests of L_1 heats 14, 15, 16, and 25, one would conclude that remelting in the cupola made the iron worse, while from the tests made under commercial conditions no definite conclusion could be drawn. However, it is plain that mere remelting is by no means a "cure-all" for blistering. The results with heats L_1, 22 and 27, suggest that an increase in the sulphur content to 0.10 to 0.12 per cent would help, but when sulphur was added in heat L_1–28 (Table 4) this conclusion was not verified.

A few heats of iron L_1 were made with additions of tin or arsenic, but no beneficial results were observed.

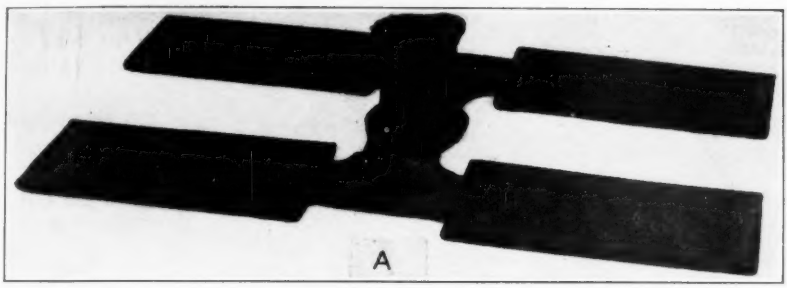
Inconclusive results were also obtained from some experiments (2-coat, wet-process enamel on iron L_1, heat 14, Table 4) in an effort to study the possibilities of surface treatment, aimed to remove carbon or graphite from the surface before enameling.

TABLE 4.—*Comparison of tests on iron with wet-process enamel*

Iron	Heat	Number of times through	Carbon			Mn	P	S	Si	Mn/S ratio	Rating	
			Total	Graphite	Combined						Bureau of Standards	Commercial firm
			P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
R_1	7, cupola	First	3.40	3.18	0.22	0.69	0.81	0.048	2.82	12.2	------	100
	13, cupola	Third	3.22	2.74	.48	.44	.84	.086	2.69	5.1	94	100
	9, electric	First	3.62	3.05	.57	.73	.80	.026	2.90	28.1	89	94
	24, electric plus S	do	3.64	3.16	.48	.74	.77	.110	2.75	6.7	100	------
	26, electric plus S	do	3.58	3.09	.49	.77	.79	.090	2.93	8.6	96	------
L_1	6, cupola	First	3.65	2.97	.68	.56	.46	.050	2.16	10.2	------	0
	14, cupola	do	3.47	3.07	.40	.57	.46	.076	2.24	7.5	72	78
	15, cupola	Second	3.51	2.74	.77	.42	.46	.083	2.07	9.2	28	56
	16, cupola	Third	3.47	2.95	.52	.33	.47	.095	1.92	3.5	0	67
	25, cupola	Fifth	3.20	.99	2.21	.18	.47	.125	1.51	1.4	0	89
	22, cupola plus S	First	3.59	2.99	.60	.56	.45	.121	2.22	4.6	100	92
	8, electric	do	3.67	3.16	.51	.62	.47	.048	2.32	13.0	0	83
	27, electric plus S	do	3.75	3.19	.56	.65	.43	.105	2.30	6.2	83	100
	28, electric plus S	do	3.67	3.09	.58	.61	.44	.092	2.21	6.6	50	56

Sand-blasted specimens of "blistering" iron were covered with commercial grades of red lead, red iron oxide, and black iron oxide, respectively, and heated to 925° C. (1,700° F.) for 10 minutes. Much of the lead oxide was volatilized during heating. After lightly cleaning the surface and enameling, no distinct or significant difference was found between the blistering of specimens so treated and that of untreated specimens.

Specimens of irons L_1, heat 17, and R_1, heat 7, were lightly sand-blasted and heated in steam for about an hour at 500° C. (930° F.), in order to produce a thin adhering coating of oxide on the surface. Part of each specimen was then lightly ground down in order to clean it from oxide and the 2-coat wet-process enamel applied over the entire surfaces. With the weakly blistering iron, R_1, the oxidized surface blistered badly, while the metallic surface was almost free from blisters. With the strongly blistering iron, L_1, both the oxidized and the metallic surfaces blistered badly.



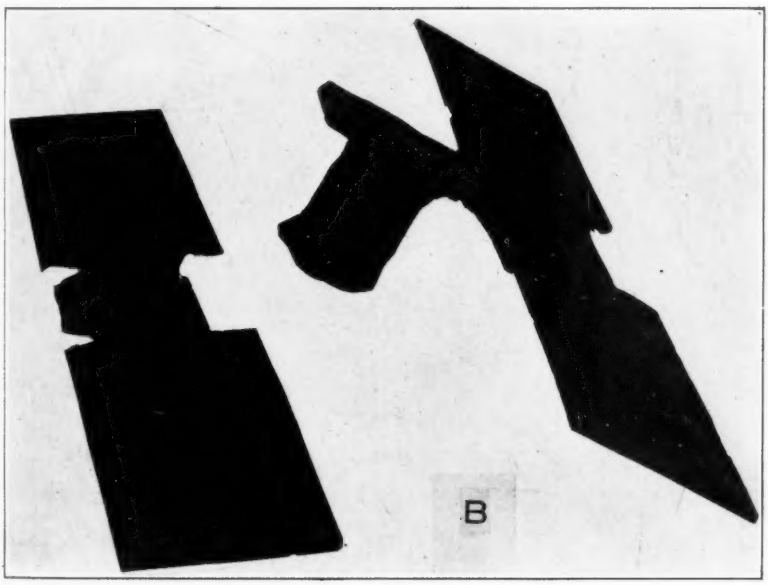


FIGURE 1.—*Specimens (3 by 6 by 3/16 inch) cast four at a time*

A, Cope side, gate in the middle; *B*, drag side of same casting

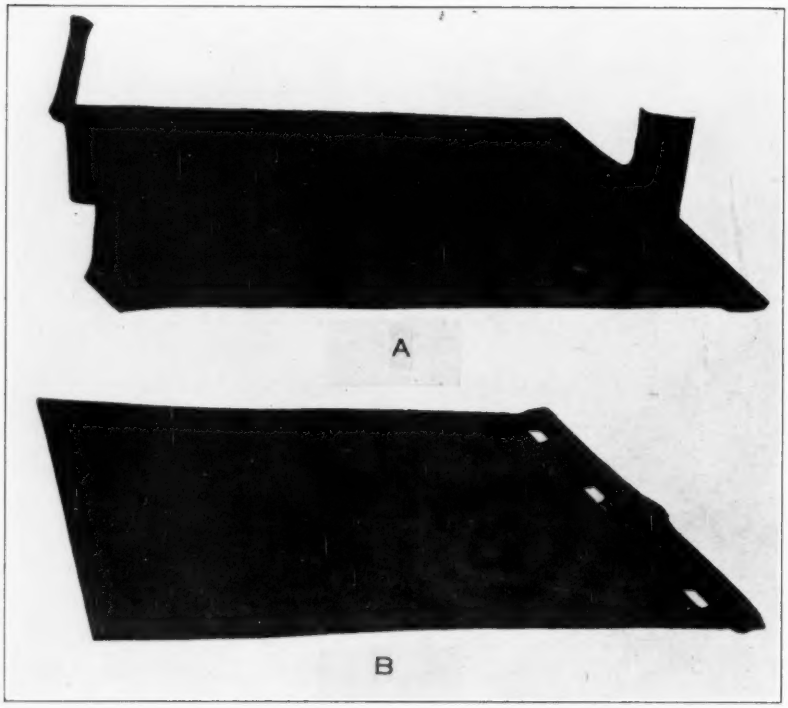


FIGURE 3.—*Specimens (3 by 6 by 3/16 inch) cast 18 in 1 plate*

A, Cope side, with gate and risers; *B*, drag side of same casting.

2. HEATING CURVE OF GROUND COAT

From a heating curve (fig. 2) of the ground coat mixture, it was evident that the firing temperature used in the early work, 900° C. (1,650° F.), was far above the sintering point of the material. Consequently the firing temperature for a number of the following tests was reduced to 760° to 800° C. (1,400° to 1,470° F.), the firing time being 12 to 15 minutes. The cover coat R–11 was fired at 680° to 710° C. (1,255° to 1,310° F.) for 6 to 9 minutes.

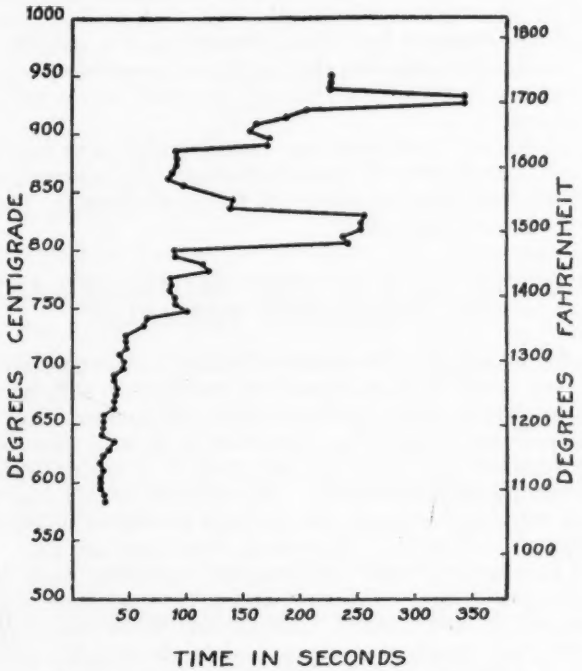


FIGURE 2.—*Inverse rate heating curve of enamel*

Ground coat powder RG–1 (+15 per cent clay). Curve shows the time required to raise the temperature of this material a certain number of degrees at different temperatures.

3. CHANGE IN FORM OF TEST PLATE

In some cases the blisters on test specimens were thought to be ascribable to porosity of the iron that might result from shrinkage near the gates, from sand holes due to washing of the sand by the stream of metal, or other causes not characteristic of the iron itself. Hence, the small separate specimens, shown in Figure 1, were replaced by a larger plate shown in Figure 3, which was later cut into specimens of the same size as Figure 1. Direct connection of a gate with a specimen was in this way eliminated. The drag side of the casting was invariably the one coated in the enameling tests. The use of the larger plate and of extreme precautions in making the molds and pouring the metal gave specimens with fewer sand holes, but erratic results still persisted on enameling.

In some cases a blister in the enamel could be logically ascribed to the presence of some flaw in the casting as shown by grinding down to the metal. The majority of blisters on specimens from the large cast plates, however, appeared to bear no relation to casting flaws.

4. CONTINUITY OF GROUND COAT

Another suggested explanation for erratic results was that perhaps the ground coat failed to cover the iron and that blisters resulted at bare spots. Specimens to which the ground coat had been applied were tested by the "ferroxyl indicator" (8). A wall of plasticine was built around the edges to hold the solution until it solidified and two copper wires were immersed in the liquid as a possible means of accelerating the action. In such a test any exposed iron is indicated by a blue precipitate.

No ground-coated specimen was found which was free from bare spots. Since various lots of "nonblistering" iron showed no blisters, it was obvious that blisters need not result necessarily from contact of the cover coat at bare spots.

III. STANDARDIZATION OF TEST PROCEDURE AND STUDY OF ADDITIONAL VARIABLES

In view of the inconclusive results obtained in the preliminary series of tests, it was decided that instead of making up a large number of specimens for distribution to commercial enamelers who would use various enamels and enameling procedures, it was best to use only one type of enamel and to do all the enameling under definitely controlled conditions at the bureau. For standardizing the enameling procedure, a supply of commercial castings known to be relatively free from blistering troubles was adopted as nonblistering iron. A standard of time and temperature was adopted for firing both the ground and the cover coat (the ground-coat and cover-coat frits were supplied by the cooperating committee). Blister-free ware was obtained with this iron when the coatings were applied in the weights prescribed.

1. METHOD OF RATING

Specimens were selected to be used in rating the enameling results numerically from 1 to 5; 1, excellent; 2, satisfactory, that is, would probably be just passed by a commercial inspector; 3, slightly blistered, probably would be rejected; 4, badly blistered; and 5, very badly blistered.

2. COMPOSITION AND APPLICATION OF ENAMEL

The enamel composition and the firing temperatures were maintained constant throughout all the rest of the investigation, though, as will be noted later, the firing periods were not. The composition and method of application of the "standard" ground and cover coats are given in Table 5.

TABLE 5.—*Composition of standard ground coat and cover coat*

Raw material	Batch weights		Calculated melted compositions		
	Ground coat	Cover coat	Ingredient	Ground coat	Cover coat
				Per cent	*Per cent*
Feldspar		34.70	SiO_2	67.40	14.30
Quartz	67.40	14.30	B_2O_3	17.04	8.91
Borax	37.10	24.30	Na_2O	8.35	7.13
Red lead	7.35	16.05	PbO	7.16	15.70
Boric acid	6.07		Feldspar		34.70
Soda niter	6.39		K_2O		1.27
Potash niter		2.73	Cryolite		4.26
Soda ash		5.47	ZnO		7.02
Fluorspar		5.47	CaO		1.23
Cryolite		4.28	CaF_2		5.47
Zinc oxide		7.02			
Whiting		2.22			
Total	124.31	116.54		99.95	100.01

The above ground and cover coats were furnished by the cooperating committee of the American Ceramic Society. The ground coat was sintered in sheet-iron pans holding about 25 pounds each in a muffle furnace for one hour at 843° to 871° C. (1,550° to 1,600° F.). The cover enamel was melted in a coal-fired open-hearth smelter in batches of about 700 pounds for about 1¾ hours.

The special ground coat used for this work was prepared by crushing the frit first in a jaw crusher, to pass a No. 4 sieve, and then milled in 10-pound batches in a 10 by 14 inch porcelain ball mill containing 46½ pounds of pebbles. The mill batch and milling procedure were as follows:

	Pounds
Frit	10
Water	5.5

This was ground three hours (12,000 revolutions), and the following addition made:

	Pounds
Water	1
Clay	1.5

This was then ground three-fourths hour (3,000 revolutions), more.

A screen test of the ground coat prepared in this way gave the following results, based on the dry weight of enamel:

	Per cent
Coarser than 115 mesh	0.04
Through 115 on 200 mesh	.03

The white cover enamel was also prepared by grinding for three hours (12,000 revolutions), in a porcelain ball mill containing 46½ pounds of pebbles in 10-pound batches as follows:

Frit	pounds	10
Clay	ounces	9.6
Tin oxide	pounds	1
Water	do	4.5

A screen test of the white cover enamel gave the following results based on dry weight of enamel:

	Per cent
Coarser than 115 mesh	0.06
Through 115 on 200 mesh	2.54

The cast-iron specimens to be enameled were prepared by sand blasting with Ottawa sand-blast sand at 25 pounds pressure and then cleaned free from dust. (The time of sand blasting was not specified at this stage of the work.)

The ground coat prepared as above was applied at a specific gravity of 1.53 to give a wet coating of 3 to 4 g on the test specimens (3 by 6 inches). These were dried in an electric oven at 90° C. for at least 45 minutes. They were then fired in a gas-fired muffle furnace at 835° C. (1,535° F.), for eight minutes (three to eight pieces in a load), and allowed to cool in the air. The temperature drop upon insertion of the load was about 45° C. (81° F.), recovery being made before the end of the firing period.

The white cover enamel was applied to the ground-coated pieces at a specific gravity of 1.91 to give a wet coating of 23 (±1) g on each specimen. The pieces were dried in an electric oven at 90° C. for at least 1½ hours. They were kept in the oven at this temperature until ready to be fired and were then fired at 790° C. (1,455° F.), for seven minutes (three to eight pieces in a load), the temperature drop upon insertion of the load in this case being about 30° C. (54° F.).

Inasmuch as the method called for handling three to eight pieces as a furnace load, in general a load was made up of specimens from different heats, not of duplicate specimens from the same heat of iron. Instead of relying on a single specimen as an indicator of blistering, four or more duplicate specimens were fired in different loads. This procedure at once brought out the fact that duplicate specimens, even under the carefully controlled firing conditions, often did not behave the same as regards the formation of blisters.

3. NEW IRONS OBTAINED

The original irons, R_1 and L_1, having been nearly exhausted in previous work, similar northern irons, R_2 (slightly blistering) and L_2 (strongly blistering) were obtained from the same sources as before. Southern and southern charcoal pig irons were also obtained for comparison.

The compositions of all of the pig irons used are shown in Table 6.

TABLE 6.—*Composition of pig irons used in enameling tests*

(See Table 16 for content of other elements)

Designation of irons	Character	Composition						
		Total carbon	Graphite carbon	Combined carbon	Mn	P	S	Si
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Southern charcoal	Weakly blistering	3.82	3.40	0.42	0.17	0.51	0.024	1.75
Southern	do	3.55	3.15	.40	.24	.82	.021	2.73
R_1	do	3.62	3.06	.56	.78	.83	.029	2.99
R_2	do	3.61	2.96	.65	.68	.78	.045	2.66
L_1	Blistering	3.81	3.15	.66	.67	.46	.045	2.31
L_2	do	3.73	3.14	.59	.78	.50	.090	2.55

4. STUDY OF SEVERAL VARIABLES—MANGANESE-SULPHUR RATIO, PHOSPHOROUS CONTENT, COMBINED CARBON CONTENT, CARBONACEOUS FACINGS

On the assumption that the average enamel rating might show the presence or absence of a trend, the ratings have been plotted against

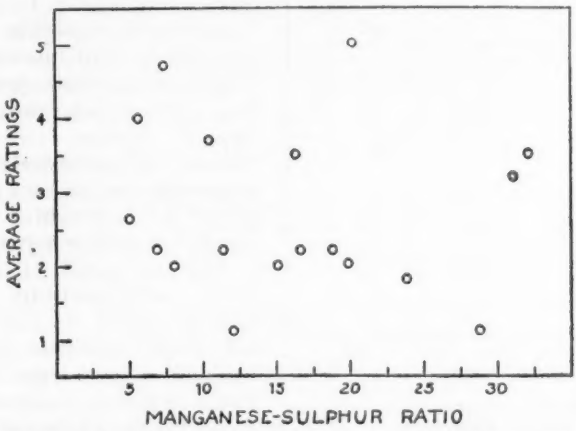


FIGURE 4.—*Average ratings plotted against manganese-sulphur ratios*

the manganese-sulphur ratio and the combined carbon in Figures 4 and 5. From the data shown in Figure 4, it appears that control of the manganese-sulphur ratio offers little promise. Figure 6 indicates that phosphorus in itself is not a major factor, since both good and bad specimens are found whether the phosphorus is present in

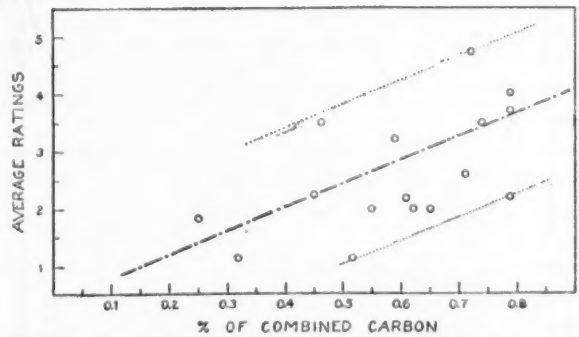


FIGURE 5.—*Average ratings plotted against per cent of combined carbon*

Heavy line indicates general trend and light lines indicate upper and lower limits.

amounts of 0.50 or 0.80 per cent. On the other hand, it does appear that as a general thing the lower the combined carbon, the less the tendency toward blistering, although in some cases high combined carbon does not appear to be detrimental. Figure 7 indicates that, other things being equal, the combined carbon falls as the silicon

increases, as is to be expected; that is, there is some indication that the softer irons (low combined carbon, high silicon) give less trouble than the harder irons.

It should be pointed out that besides the variables plotted in these figures there are other variables, which are neglected in the figures. For instance, in Figure 6, the position of the points is influenced by the combined carbon content as truly as they are in Figure 5, but the combined carbon content is neglected in Figure 6. Hence, the figures should be considered only as approximate indications of the effect of individual elements upon blistering tendencies.

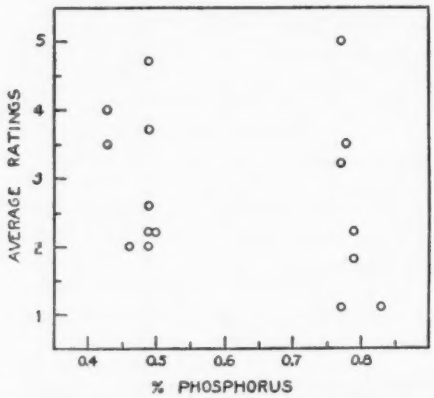


FIGURE 6.—*Average ratings plotted against per cent of phosphorus*

Various mold facings were tried, as shown in Table 7. Heats 48, 50, 51, 52, and 53, all with carbonaceous mold facings, ranged from 2.3 to 3.5 average rating. A proprietary mold facing was suggested as a possible cure for blisters. This facing was of complex composition and contained much carbonaceous material. When this was used on parts of molds, the corresponding parts of the castings, when enameled, were found to blister excessively, regardless of the iron used; whereas the parts that had been in contact with the uncoated mold blistered only slightly or not at all, depending on the iron. It may be pointed out, however, that a light application of plumbago seemed to be rather beneficial in the case of heat 51.

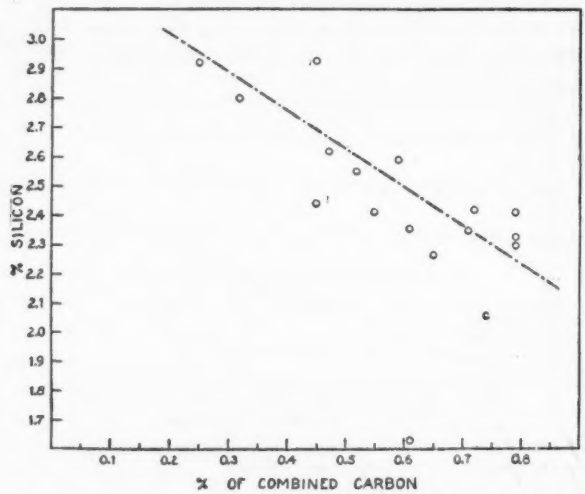


FIGURE 7.—*Per cent of silicon plotted against per cent of combined carbon*

TABLE 7.—*Composition and enameling results of a number of heats of iron*

Iron	Furnace and melt	Additions	Heat No.	Approximate pouring temperatures	Composition									Mn/S ratio	Enamel rating, load No.							
					Carbon			Mn.	P	S	Si	Cr			0	1	2	3	4	5	6	Average
					Total	Graphite	Combined															
				°C.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*										
Southern charcoal.	Electric, first	None	42	1,400	3.61	2.99	0.62	0.18	0.49	0.023	1.63	0.03		8	1	4	1	---	2	2	---	2.0
Southern	do	do	41	1,400	3.46	3.14	.32	.24	.83	.020	2.80	.10		12	1	1	1	---	2	1	---	1.1
R_1	do	do	45	1,390–1,375	3.47	3.22	.25	.76	.79	.032	2.92	------		23.7	3	1	2	---	2	1	---	1.8
R_1	do	Sulphur	35	1,390–1,370	3.54	3.09	.45	.77	.79	.115	2.93	------		6.7	3	2	2	2	---	---	---	2.2
R_1	Electric, second	Scrap from 35 plus Mn.	36	1,405–1,380	3.46	2.57	.89	2.00	.77	.100	2.60	------		20	5	5	5	5	---	---	---	5.0
R_2	Electric, first	None	43	1,400–1,375	3.40	2.88	.52	.60	.77	.021	2.55	------		28.6	1	2	1	---	1	1	---	1.1
R_2	do	do	30	1,400	3.66	3.19	.47	.64	.78	.020	2.62	------		32	4	3	3	4	---	---	---	3.5
R_2	Electric, second	do	32	1,400–1,390	3.62	3.03	.59	.62	.77	.020	2.59	------		31	4	4	4	1	---	---	---	3.2
L_1	Electric, first	do	46	1,400–1,375	3.72	3.07	.65	.66	.46	.044	2.27	------		15	4	1	1	---	3	1	---	2.0
L_1	do	Sulphur	33	1,400	3.81	3.02	.79	.64	.43	.115	2.30	------		5.6	4	4	4	4	---	---	---	4.0
L_1	Electric, second	Scrap from 33 plus Mn.	34	1,400	3.75	3.01	.74	1.50	.43	.095	2.06	------		15.8	4	4	2	4	---	---	---	3.5
L_2	Cupola, first	None	37	1,310–1,290	3.69	2.90	.79	.67	.49	.065	2.41	------		10.2	4	5	5	3	3	2	---	3.7
L_2	Cupola, first, heated in electric.	do	38	1,400–1,390	3.64	2.85	.79	.65	.49	.055	2.33	------		11.8	1	3	1	2	3	3	---	2.2
L_2	Cupola, first	Sulphur	39	----------	3.76	3.04	.72	.62	.49	.085	2.42	------		7.3	5	5	5	5	4	4	---	4.7
L_2	Cupola, first, heated in electric.	do	40	1,420	3.66	2.95	.71	.60	.49	.120	2.35	------		5.0	3	2	3	2	2	1	---	2.6
L_2	Electric, first	None	44	1,400–1,375	3.60	3.15	.45	.71	.49	.043	2.44	------		16.5	4	3	1	---	2	1	---	2.2
L_2	do	do	29	1,400–1,380	3.63	3.08	.55	.79	.49	.040	2.41	------		19.8	3	2	2	1	---	---	---	2.0
L_2	Electric, second	do	31	1,400–1,380	3.64	3.03	.61	.75	.50	.040	2.36	------		18.8	2	4	2	1	---	---	---	2.2
L_2	Electric, first	do	47	1,400	(1)										---	4	4	4	3	4	1	3.3
L_2	do	do	49	1,400–1,390	(2)										---	3	1	3	2	1	1	1.8
L_2	do	do	48	1,415–1,400	(3)										---	2	4	4	3	2	2	2.8
L_2	do	do	53	1,400	(4)										---	5	4	4	4	2	1	3.3
L_2	do	do	50	1,440	(5)										---	4	4	4	3	3	3	3.5
L_2	do	do	52	----------	(5)										---	1	4	3	2	3	3	2.7
L_2	do	do	52	1,400	(6)										---	2	5	1	3	3	3	2.8
L_2	do	do	51	1,400	(6)										---	2	3	3	3	1	2	2.3

[1] Not analyzed; no mold facing.
[2] Not analyzed; silica flour facing.
[3] Not analyzed; ethylene glycol spray facing.
[4] Not analyzed; ethylene glycol and silica facing.
[5] Not analyzed; wheat flour facing.
[6] Not analyzed; plumbago.

5. NONBLISTERING IRON BECOMES BLISTERING ON REMELTING

A need having arisen for more specimens of known "nonblistering" iron, some commercial castings which were left from the stock used in a study of enamels at the Bureau of Standards (4), and which were considered free from any tendency to blister, were remelted in the electric furnace and cast into standard test plates. On enameling these castings by the standard method they blistered badly. This again raised the question whether irregularities in results should be attributed to the iron or to some unconsidered variable in the enameling process.

6. "BAKING" PROCESS AND WATER ADSORPTION TESTS

The idea of preheating at a low temperature (termed "baking" to distinguish it from the "burning-out" process) was tried out. Since enamel is applied wet and contains uncalcined clay to hold it in suspension, it appeared possible that the water of constitution of the clay which would not be driven off in drying, might react during the firing process and be a cause of blisters. It was also considered possible that water might be firmly adsorbed in microscopic or submicroscopic "pores" of the metal, since an adsorption of moisture during pickling, which is not given off on drying but is given off at galvanizing temperatures, has been suggested by Lindemuth (9) as a possible cause for blistering of galvanized sheet. The details and effects of the baking treatment are discussed in one of the following sections.

In order to study the hypothesis that water adsorbed in pores might play a part, seven specimens each of the two irons, R_2 and L_2, were sand-blasted and then soaked in water 40 hours, after which they were wiped with a towel, sprayed with ground coat in the regular manner, and put through the "range" test. (See following section.) The results are shown in Figure 8, and should be compared with the lower halves of the specimens in Figure 9, which were not water-soaked. The weakly blistering iron, R_2, was not affected by the water-soaking treatment, but the strongly blistering iron, L_2, appeared to be somewhat more blistered on the three and five minute ground-coat firings with water-soaking than without.

IV. THE RANGE METHOD OF FIRING AND ITS APPLICATIONS

In the attempt to make the "standard" enameling process a sharper "indicator" so that a laboratory test would more clearly show whether a given metallurgical change in composition or treatment of the cast-iron had affected its blistering properties favorably or adversely, a new test was developed.

The basis of the new test was that each iron should be enameled under a variety of firing treatments instead of a single one, and that irons should be distinguished from each other according to the breadth of the range of treatments within which no blisters were observed. Seven specimens were required to make a test and, for the particular enamels which had been supplied the bureau, the following schedule was used:

The ground coat was fired at 875° C. (about 1,605° F.) for varying lengths of time on different specimens. The first specimen was fired

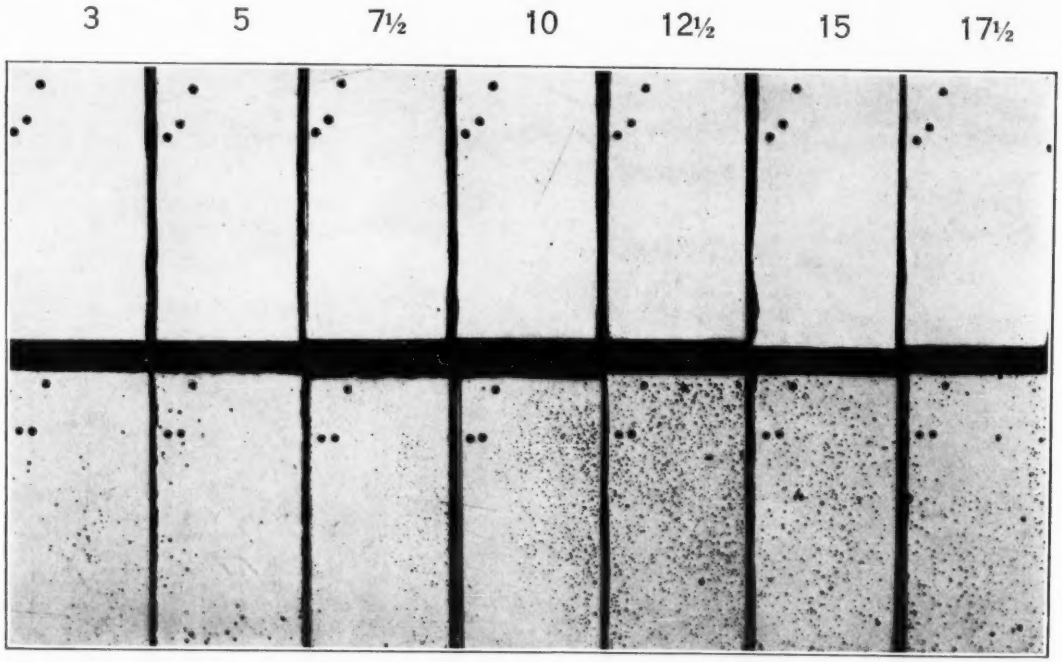


FIGURE 8.—*Blistering behavior of irons L_2 and R_2*

Numbers indicate minutes of firing ground coat at 875° C. (1,605° F.). Cover coats all fired 8 minutes at 800° C. (1,470° F.). Top row is iron R_2 and bottom row iron L_2. These specimens were all water soaked before enameling, but are fairly typical also of results obtained without water soaking. The large black spots in the upper left corner in this and succeeding figures are holes drilled in the iron specimens for identification purposes.

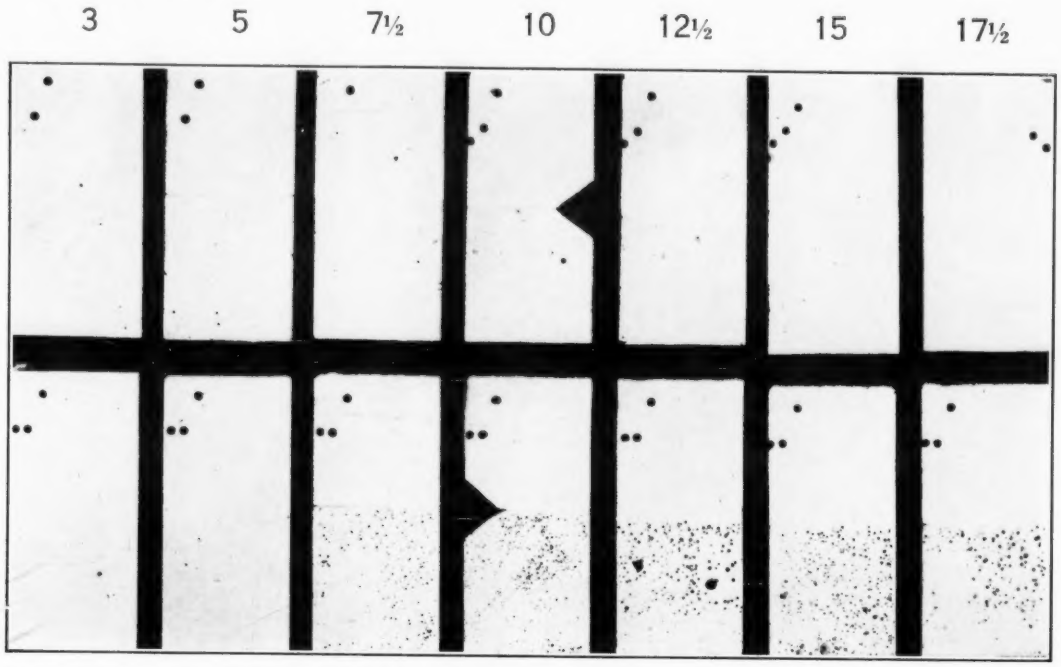


FIGURE 9.—*Effect of machining off original iron surface*

Surfaces of ends of plates bearing identification holes machined off before enameling. Top row iron R_2 and bottom row iron L_2. Numbers indicate minutes of firing ground coat at 875° C. (1,605° F.). Cover coats all fired 8 minutes at 800° C. (1,470° F.).

for 3 minutes, the second 5 minutes, the third 7½ minutes, and so on by 2½-minute increments, the seventh specimen being fired 17½ minutes. Then the cover coat was applied to all under uniform conditions and fired for 8 minutes at 800° C. (about 1,470° F.). Except for the firing periods, and the specification of 3.0 to 3.6 g of wet ground instead of 3.0 to 4.0 g, the conditions of application as worked out in the standard process were retained.

Different lots of castings reacted to this test in various ways. One lot might give the best results when the ground coat was fired for five minutes and another when it was fired for seven and a half minutes, while a third would be almost free from blisters throughout the range of treatments. It then became apparent that no single-firing treatment could fairly be chosen as standard.

Looking at the bottom half of each of the two sets of comparison plates in Figure 9, one will note that, at five minutes' firing of the ground coat, the specimen in the bottom row would be called superior to that in the upper row, whereas at seven and a half minutes' firing, the opposite is very clearly shown. The whole series shows unmistakably that the upper row is the better.

Blistering may be considered as a gas-producing reaction between the metal and the enamel, or the air. This reaction requires time. A metal that can be heated over a wide range of firing periods without blistering is obviously better than one which is equally free from blistering at one definite condition of firing, but will blister if that condition is not adhered to.

A few check tests were made on specimens from heats of iron which had previously been enameled by the standard procedure. It was found that the check specimens gave quite different results when the ground coat was fired under different conditions. This observation may help to explain some of the erratic results of early tests both at the bureau and at the cooperating plants.

V. FURTHER COOPERATIVE EXPERIMENTS

1. OUTLINE OF PROCEDURE

After some preliminary tests, it was decided to submit the two irons, R_2 and L_2, to cooperative tests at the bureau and at two commercial laboratories. The specimens and the enamels were distributed from the bureau and the process of application which has been given in the description of the range test was used in these cooperative experiments. In addition, a high lead enamel without a ground coat was applied under the conditions which are given in Table 8.

TABLE 8.—*High lead enamel*

[Applied as two coats, without ground coat]

Batch weights		Calculated composition after melting	
Raw material	Parts	Ingredient	Parts
	Per cent		*Per cent*
Canadian feldspar	19.90	Feldspar	19.90
Flint	12.20	SiO_2	12.20
Borax	21.05	Na_2O	5.43
Red lead	35.30	B_2O_3	8.97
Fluorspar	10.02	PbO	34.60
Cryolite	3.34	CaF_2	10.02
Soda niter	5.52	Cryolite	3.34
Zinc oxide	5.53	ZnO	5.53
Boric acid	2.19		
Total	115.05		99.99

		Mill batch	
		Ingredient	Parts by weight
Canadian feldspar:	*Per cent*		
SiO_2	64.70		
Fe_2O_3	.02	Frit	100
Al_2O_3	19.16	Clay	3
Na_2O	1.98	Tin oxide	6
K_2O	12.95	Water	45
Ignition loss	.75		

The slip (enamel suspension) was made up to a specific gravity of 2.15 and sprayed on the castings, the wet coating, weighing 6.0 to 6.6 g per specimen. After drying at not less than 90° C. (195° F.) for not less than an hour the plates were fired at 710° C. (1,310° F.). The temperature of the furnace regained its original value in five minutes after insertion of the load. Seven sets were fired, the initial firing period being 10 minutes, which was increased by 2½-minute increments up to 25 minutes for successive firings. The second coat (20 to 22 g per specimen) was sprayed on, dried as before, and fired at 660° C. (1,220° F.) for 12 minutes.

In these cooperative experiments some tests of the baking treatment mentioned above were included. In one set of tests the baking was done on the ground coat only, in another both ground and cover coats were baked, and in the third only the cover coat. Baking was always carried out in a furnace at 500° C. (930° F.) for a period of eight minutes and the ground coats were all fired in seven and one half minutes. For these tests, including those on baking, four electric furnace heats of the two irons, R_2 and L_2, were made, a total of 1,440 specimens being prepared.

2. RESULTS OBTAINED

The results of these tests and the chemical compositions of the irons, are given in Tables 9 and 10, respectively.

TABLE 9.—*Results of cooperative enameling tests carried out at the bureau and in two commercial laboratories*

RATINGS OF SPECIMENS HAVING GROUND COATS FIRED FOR DIFFERENT PERIODS

Enameling procedure	3 minutes	5 minutes	7½ minutes	10 minutes	12½ minutes	15 minutes	17½ minutes	Average ratings	3 minutes	5 minutes	7½ minutes	10 minutes	12½ minutes	15 minutes	17½ minutes	Average ratings
	Iron L_2 (heat 1–55)								Iron L_2 (heat 2–55)							
Electric furnace, Bureau of Standards	5	3	5	5	5	5	5	4.7	5	2	5	5	5	5	5	4.6
Gas furnace, Bureau of Standards	5	5	4	5	5	5	5	4.9	3	2	3	5	5	5	5	4.0
Gas furnace, commercial laboratory No. 1	4	4	5	5	5	5	5	4.7	5	4	5	5	5	5	5	4.9
Electric furnace, commercial laboratory No. 2	5	4	5	5	5	5	4	4.7	4	4	3	5	5	5	5	4.4
Average grading	4.8	4.0	4.8	5.0	5.0	5.0	4.8	4.8	4.3	3.0	4.0	5.0	5.0	5.0	5.0	4.5
	Iron L_2 (heat 3–55)								Iron L_2 (heat 4–55)							
Electric furnace, Bureau of Standards	3	3	2	5	5	5	5	4.0	5	2	3	4	1	2	4	3.0
Gas furnace, Bureau of Standards	4	1	2	5	5	5	5	3.9	5	2	1	3	4	3	4	3.1
Gas furnace, commercial laboratory No. 1	3	4	5	5	5	5	5	4.6	2	3	3	4	5	4	3	3.4
Electric furnace, commercial laboratory No. 2	3	2	3	3	4	4	4	3.3	3	3	2	3	3	2	3	2.7
Average grading	3.3	2.5	3.0	4.5	4.8	4.8	4.8	4.0	3.8	2.5	2.3	3.5	3.3	2.8	3.5	3.1
Grand average of all																4.1
	Iron R_2 (heat 1–56)								Iron R_2 (heat 2–56)							
Electric furnace, Bureau of Standards	5	4	5	5	5	5	5	4.8	4	1	2	2	3	1	1	2.0
Gas furnace, Bureau of Standards	2	2	2	3	2	3	4	2.6	1	1	2	2	1	3	3	1.8
Gas furnace, commercial laboratory No. 1	4	4	5	5	5	3	------	4.3	2	3	3	4	3	------	3	3.0
Electric furnace, commercial laboratory No. 2	5	4	3	4	5	5	3	4.1	5	1	2	3	3	3	3	2.8
Average grading	4.0	3.5	3.8	4.3	4.3	4.0	4.0	3.9	3.0	1.5	2.3	2.8	2.5	2.3	2.5	2.4
	Iron R_2 (heat 3–56)								Iron R_2 (heat 4–56)							
Electric furnace, Bureau of Standards	4	1	4	3	3	3	1	2.7	5	5	4	5	3	3	4	4.1
Gas furnace, Bureau of Standards	1	1	2	2	2	3	3	2.0	1	2	3	1	2	4	4	2.4
Gas furnace, commercial laboratory No. 1	2	2	3	3	3	3	3	2.7	3	4	5	5	5	5	5	4.6
Electric furnace, commercial laboratory No. 2	3	1	2	3	3	2	1	2.1	4	2	2	4	5	4	5	3.7
Average grading	2.5	1.3	2.8	2.8	2.8	2.8	2.0	2.4	3.3	3.3	3.5	3.8	3.8	4.0	4.5	3.7
Grand average of all																3.1

TABLE 9.—*Results of cooperative enameling tests carried out at the bureau and in two commercial laboratories*—Continued

RATINGS OF SPECIMENS BAKED AT 800° C. FOR 8 MINUTES WITH ENAMEL ON BEFORE FIRING

Enameling procedure	Baked—			Baked—			Baked—			Baked—			Baked—			Grand average
	Ground coat	Cover coat	Ground and cover coats	Ground coat	Cover coat	Ground and cover coats	Ground coat	Cover coat	Ground and cover coats	Ground coat	Cover coat	Ground and cover coats	Ground coat	Cover coat	Ground and cover coats	
	Iron L_1 (heat 1-55)			Iron L_1 (heat 2-55)			Iron L_1 (heat 3-55)			Iron L_1 (heat 4-55)			Average rating			
Baked in electric furnace; fired in gas furnace, Bureau of Standards	1	3	3	2	1	2	1	2	1	1	1	1	1.3	1.8	1.8	.....
Baked and fired in gas furnace, commercial laboratory No. 1	5	5	5	5	5	5	5	5	5	4	3	4	4.8	4.5	4.8	.....
Baked and fired in electric furnace, commercial laboratory No. 2	3	3	3	2	2	3	4	3	3	3	2	3	3.0	2.5	3.0	.....
Grand average	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	3.0	2.9	3.2	[1] 3.0
	Iron R_1 (heat 1-56)			Iron R_1 (heat 2-56)			Iron R_2 (heat 3-56)			Iron R_2 (heat 4-56)			Average rating			
Baked in electric furnace; fired in gas furnace, Bureau of Standards	2	3	1	1	1	1	1	2	3	1	1	2	1.3	1.8	1.8	.....
Baked and fired in gas furnace, commercial laboratory No. 1	4	3	3	3	1	1	3	3	2	4	3	3	3.5	2.5	2.3	.....
Baked and fired in electric furnace, commercial laboratory No. 2	3	2	3	3	1	2	3	1	3	4	2	3	3.3	1.5	2.8	.....
Grand average	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	2.7	1.9	2.3	[2] 2.3

[1] This average rating of 3.0 is to be compared with the average of iron L_2, unbaked, at 7½ minutes only (3.5).
[2] This average rating of 2.3 is to be compared with the average of iron R_2, unbaked, at 7½ minutes only (3.1).

TABLE 10.—*Results of analyses of different heats of irons L_2 and R_2*

Heat No.	Iron	Approximate pouring temperatures	Composition							
			Carbon			Mn	P	S	Si	Cr
			Total	Graphite	Combined					
		° C.	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
1–55	L_2	1,410–1,388	3.40	2.93	0.47	0.72	0.555	0.035	2.37	0.04
2–55	L_2	1,380	3.54	3.06	.48				2.34	
3–55	L_2	1,390	3.46	2.94	.52				2.39	
4–55	L_2	1,400	3.36	3.10	.26	.72	.515	.039	2.30	.04
1–56	R_2	1,398	3.13	2.94	.19				2.53	
2–56	R_2	1,398	3.48	3.10	.38	.61	.790	.027	2.22	.03
3–56	R_2	1,388	3.39	3.11	.28				2.51	
4–56	R_2	1,380–1,350	3.45	3.08	.37				2.45	.04

Two factors which are very important stand out clearly from the results of these cooperative tests. First, there is a difference in the tendencies of different lots of iron to produce blisters when enameled under uniform conditions. Second, different heats of the same pig iron may vary in their blistering tendencies just as definitely as heats from different pig irons do. Table 9 shows that there are four heats of each iron and four sets of testing conditions for each heat (two commercial laboratories and two different types of furnaces at the bureau). The average ratings under these four sets of conditions agreed very well in placing the different sets of castings in order of blistering tendency. Thus, for the four heats of iron L_2, heat 4–55 was first (in order of increasing blistering tendency) in all four cases. Heat 3–55 was second in all four cases. Heat 2–55 was third in three out of four cases, and fourth in the remaining case. Heat 1–55 was at the bottom of the list (greatest blistering tendency) in three out of four cases, and next to the bottom in the other one case. For iron R_2 there was unanimous agreement that heats 2–56 and 3–56 are both better than either 1–56 or 4–56. The former two heats were evenly divided between first and second places. Heat 4–56 received third place in three out of four cases, and fourth place in the remaining case. Heat 1–56 received the lowest rating in three out of four cases, and next to the lowest in the other case. The average ratings (Table 9) showed that heat 4–55 has so much less blistering tendency than the other three heats of iron L_2 that it may be classed separately from them. Likewise, heat 1–56 has considerably more blistering tendency on the average than the other three heats of iron R_2. The superiority of iron R_2 over L_2, with respect to blistering tendency, is quite marked in the remaining six heats.

Commercial laboratory No. 2 as a rule produced specimens not so badly blistered as laboratory No. 1. In this connection it is significant (in view of the results reported later) that laboratory No. 2 used a commercial sand-blasting outfit with 90 pounds air pressure (firing in an electric furnace) while laboratory No. 1 used a laboratory sand blast at a considerably lower air pressure (firing in a gas furnace).

The data discussed above all apply to the process and enamels adopted as standard. Practically no information was gained from the low fusion, high lead enamel test, for very little difference was shown between the different lots of castings with this enamel.

The results obtained with the baking tests varied according to the laboratory in which the tests were made. Since in the baking tests the ground coats were all fired seven and one-half minutes (875° C., about 1,605° F.), it seems logical to compare the baked specimens with only those unbaked ones which had the same firing treatment. The data in Table 9, when analyzed in this way, show that in the bureau tests baking was distinctly beneficial, and that baking of the ground coat only caused greater improvement than any other baking procedure.

The results of some additional tests on baking which were carried out at the bureau, but not duplicated in the two cooperating laboratories, are given in Table 11.

TABLE 11.—*Results of enameling tests on heat No. 44, iron L_2 after baking*

[Ratings of specimens having ground coats fired for different periods]

	3 minutes	5 minutes	7½ minutes	10 minutes	12½ minutes
Ground coat and cover coat baked 8 minutes at 500° C. (930° F.)	3	3	2	3	3
	3	4	4	4	2
		[1] 3			
		[1] 1			
Average	3	2 7	3	3.5	2.5
Not baked	5	4	3	4	4
	5	4	4	5	5
		[1] 2			
		[1] 4			
Average	5	3.5	3.5	4.5	4.5

[1] Duplicate.

The results of the above-tabulated baking tests and the tests of all three laboratories considered as a whole, indicate that baking is helpful under some conditions, and if properly worked out in any particular case would doubtless constitute an added factor of safety, but that this treatment can not be relied upon to eliminate blistering.

VI. EFFECT OF THE SURFACE LAYERS OF CASTINGS ON THEIR ENAMELING PROPERTIES

1. IMPORTANCE OF CLEANING OPERATION

From microscopic data on hand at an early stage of the investigation, it was suspected that the source of trouble might be located in the surface layer and that the removal of this would eliminate blistering. A systematic investigation was not carried out at that time, because of the negative results which were obtained with some of the specimens, the surface of which had been machined and sand-blasted before enameling.

The importance of the cleaning operation was again brought up and given serious consideration on account of more recent observations showing that prolonged sand-blasting resulted in a noticeable improvement, although the normally cleaned specimens showed no indication of improper sand-blasting. This question of the proper cleaning of cast-iron ware to be enameled has been very strongly emphasized in recent literature (5). In this connection it may be

noted that variations in air pressure, reuse of old sand with large proportions of material too fine to produce effective cleaning, and changes in amount and velocity of sand due to wear of the sand-blast nozzle may pass unnoticed, so that equal removal of the surface of the castings during sand-blasting may not be obtained with equal time of blasting. Similarly if a skin of burned-on molding sand is present, the early period of the sand-blasting process will be occupied in removing the sintered sand rather than in cleaning the surface of the iron itself.

2. SURFACE REMOVAL ELIMINATES BLISTERS

Experiments were made in which the surface of each casting was machined off across one end, the other end receiving only the regular sand-blasting. Specimens prepared in this way were given the range of firing treatments which has been described. Specimens from one of the better heats of iron R_2 and of the blistering heats of iron L_2 were used. The unmachined ends of the specimens showed the usual result, namely, that iron R_2 gave very few blisters under any of the treatments, whereas iron L_2 blistered throughout the greater part of the range. (Fig. 9.) On the other hand, the machined ends of both sets of castings were relatively free from blisters throughout the range of treatments, even when the ground coat firing period was as long as 17½ minutes. Out of 37 tests, with this firing period, on unmachined specimens of irons R_2 and L_2, only three specimens had been given ratings better than 3. It was found also in a limited number of tests that the pickling of normally sand-blasted specimens with 12 per cent hydrochloric acid for 10 minutes at 60° C. (140° F.) was almost, if not quite, as effective in eliminating blisters from iron L_2 as the machining. Thus, prolonged sand-blasting, pickling, and machining removed the surfaces of the castings, and in doing so removed the source of blistering.[2]

Since each of the treatments mentioned above lightened to some extent the treated portions of the castings and caused a more rapid rise in temperature when placed in the furnace, the following experiments were made to determine whether or not the improvement of the treated ends of the castings was related to this condition.

A set of castings was planed off at one end on the opposite side from that enameled and given the regular range of enameling treatments. In this case the thin ends of the castings were no better than the thick ends, a result which indicated that the improvement above can not be attributed to the effect of decreased thickness of the castings upon the rate of heat absorption.

In order to get an idea how deep this "blistering" layer extends, specimens of iron L_2, after normal sand-blasting (which did not remove all the "blistering" layer) were machined at a slight angle to the surface to be enameled. Since the plates were not perfectly flat, the machined areas were somewhat irregular in shape. Figure 10 shows how the removal of an extremely thin layer sufficed to remove

[2] After publication of this statement in a progress report (J. Am. Cer. Soc., **11**, No. 8; August, 1928), information was received from several sources that some blistering irons were encountered in regular production which were not improved by removal of the surface layer. These reports were not received in time to do any investigative work of which the results could be included in the present paper. If blistering was due in these cases to defects such as sponginess in the castings, marked improvement would not be expected from removal of the surface layer.

the material responsible for blistering. It will be noted that blistering disappeared entirely at the boundary of the machined surface.

Whereas previous study had been directed primarily at the chemical composition and physical soundness, the work was now concentrated on the surface layers of the castings.

A more carefully controlled sand-blasting procedure was used in the subsequent work, to minimize any irregularities in results arising from variations in sand-blast treatment. Ottawa silica sand (20 to 30 mesh) was delivered at 60 pounds pressure, from a nozzle of 1 inch inside diameter, normal to the surface of the specimens placed 4 inches below for a period of 45 seconds. The specimens were moved horizontally during sand-blasting, and when an occasional specimen having less than the usual 18 square inch surface was blasted, a proportionally shorter period of blasting was used.

3. ADDITIONS OF SOFTENING AGENTS, ALSO PHOSPHOROUS AND FUSED SODIUM CARBONATE

On the theory that a softer (lower combined carbon) iron might be less "blistering" and more susceptible to removal of the surface layer in an ordinary cleaning process, an attempt was made to improve iron L_2, the more strongly blistering one, by softening it. Since an increase in the silicon or nickel contents would tend to produce this result, one-half per cent of each element was added separately and the "range" method applied. (See Table 12.)

TABLE 12.—*Effects of nickel and silicon additions on ratings of iron L_2 (electric furnace melts)*

Addition	Heat	Composition							
		Carbon			Mn	P	S	Si	Ni
		Total	Graphite	Combined					
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
None	[1] 1-2-3-4-55								
Do	61	3.26	2.78	0.48				2.12	
½ per cent Ni	57	3.25	3.14	.11	0.73	0.52	0.043	2.27	.51
Do	[2] 63								
½ per cent Si	60	3.25	2.83	.42				2.56	

Addition	Heat	Standard enamel rating at firing time shown (minutes)						
		3½	5	7½	10	12½	15	17½
None	[1] 1-2-3-4-55	4.4	2.5	3.1	4.6	4.4	4.4	[3] 4.7
Do	61		2	3	3	3	3	3
½ per cent Ni	57	2.0	2.0	2.3	2.3	3.0	3.3	[4] 4.0
Do	[2] 63		2	3	3	4	3	5
½ per cent Si	60		1	2	3	4	3	3

[1] See Table 10.
[2] Not analyzed.
[3] Average of Bureau of Standards tests in Table 9 for all four heats, without baking.
[4] Average of three sets of tests at bureau.

The results, compared with those of Table 9 over the important firing range of 5 to 10 minutes, appear promising since none of the softened irons were rated lower than grade 3 over this range, while in Table 9 half of the L_2 specimens tested at the bureau over this

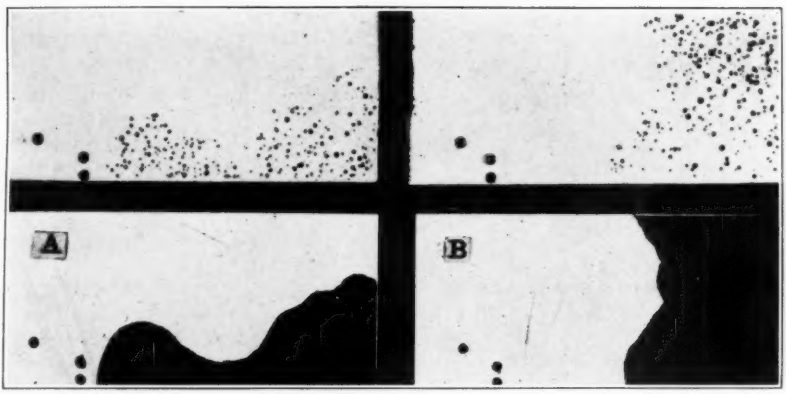
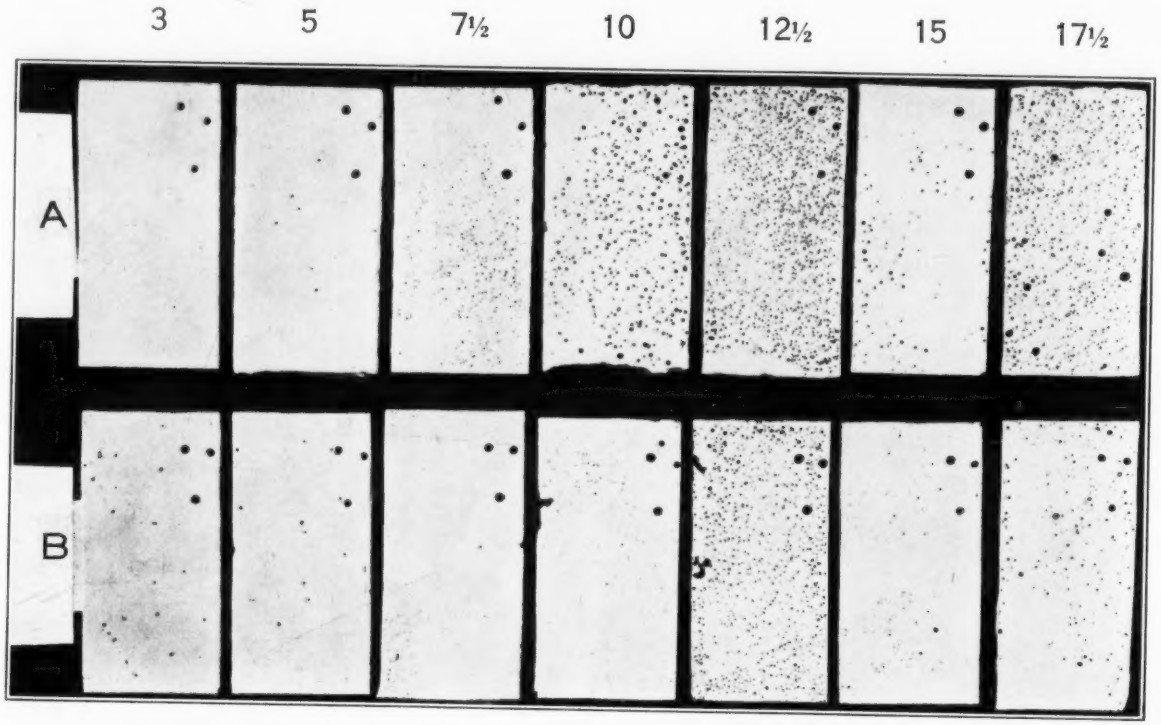


FIGURE 10.—*Plates machined off at slight angle before enameling. Iron L_2, melts 2–55 and 3–55*

Lettered plates are graphical representations of appearance of plates after machining. Unshaded portions were machined; shaded portions had normal sand-blasted surfaces. Ground coat fired 10 minutes at 875° C. (1,605° F.) and cover coat 8 minutes at 800° C. (1,470° F.).


3
5
7½
10
12½
15
17½
A
B

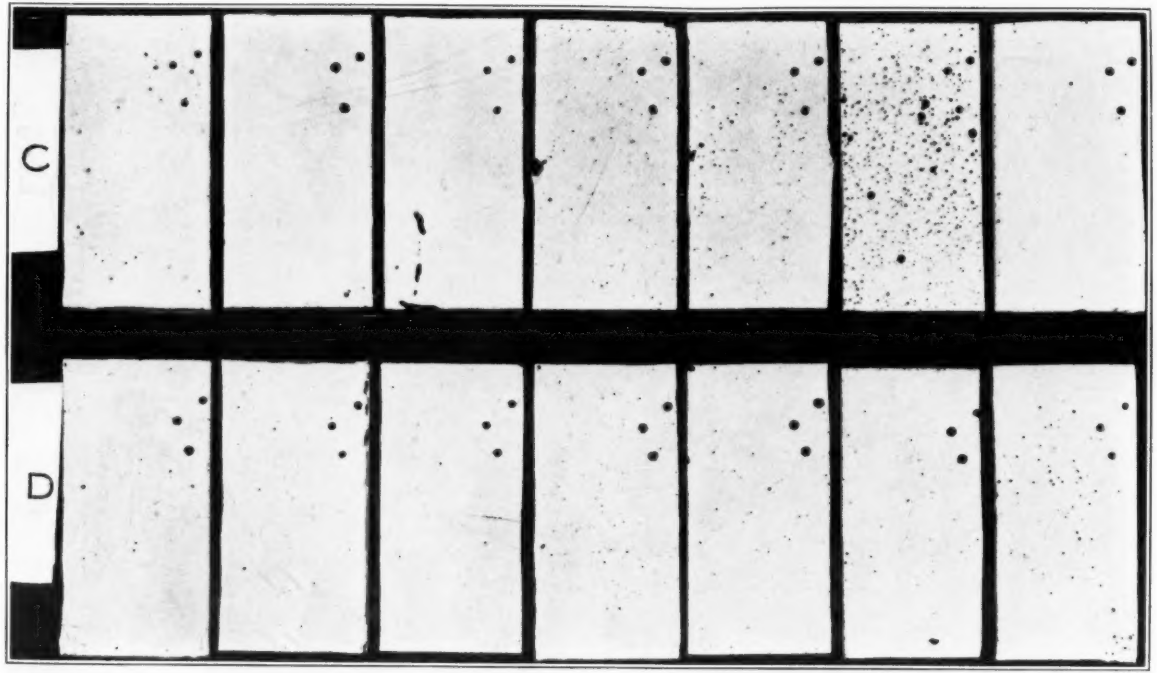
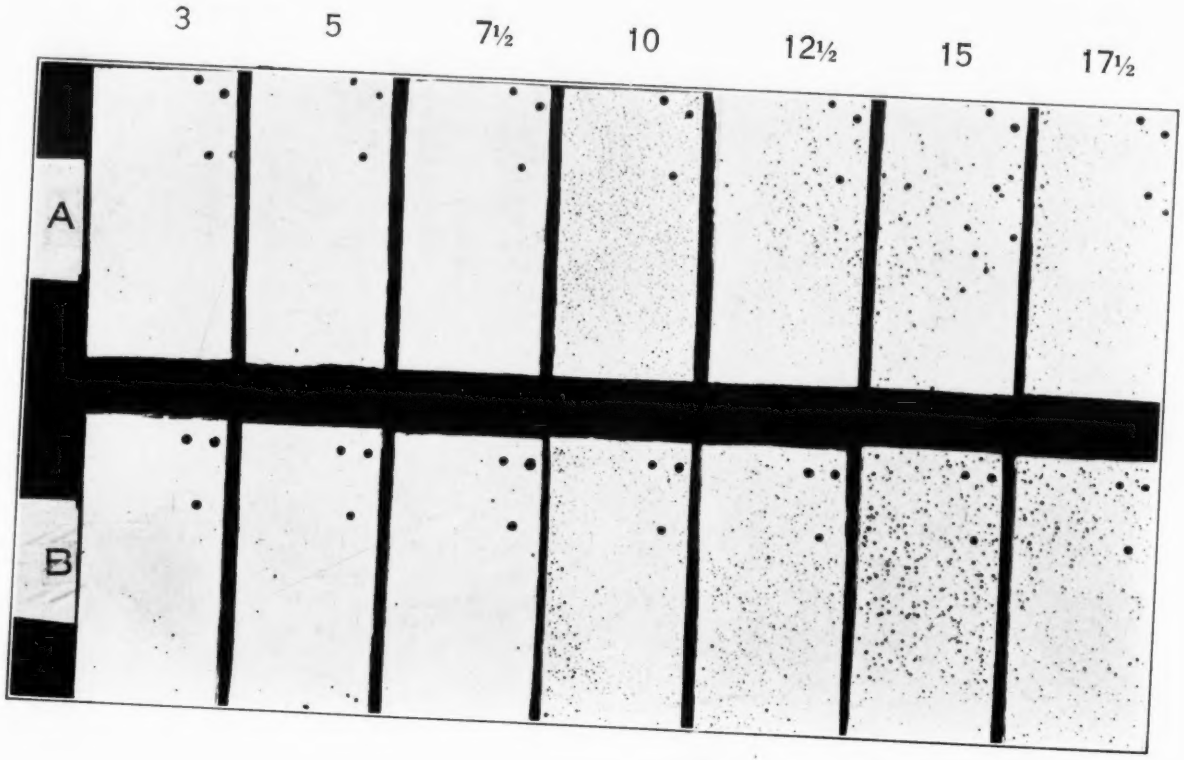


FIGURE 11.—*Effect of silicon additions on blistering tendency*

A, 2.32 per cent Si; *B*, 2.51 per cent Si; *C*, 2.65 per cent Si; and *D*, 2.92 per cent Si. Average of two determinations, Table 13. Numbers indicate minutes of firing ground coat at 875° C. (1,605° F.); cover coats all fired 8 minutes at 800° C. (1,470° F.).


3
5
7½
10
12½
15
17½
A
B

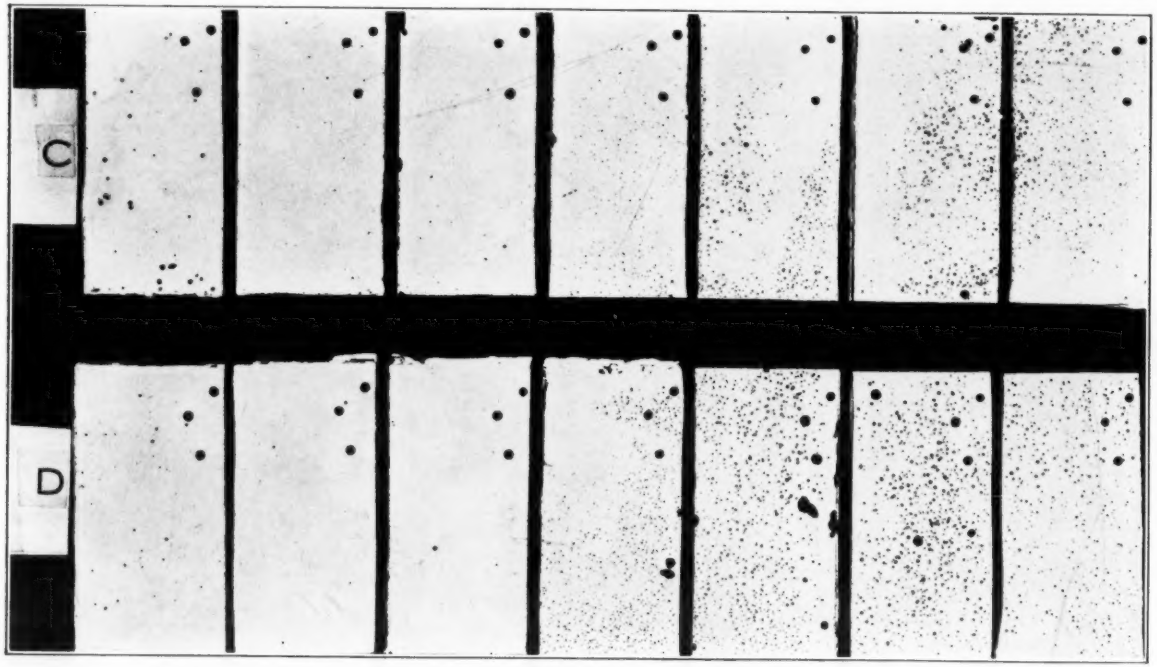


FIGURE 11½.—*Effect of additions of chromium up to 0.1 per cent*

No analysis for chromium was made, but amounts added were: *A*, no Cr added; *B*, 0.03 per cent Cr; *C*, 0.05 per cent Cr; and *D*, 0.1 per cent Cr. Numbers indicate minutes of firing ground coat at 875° C. (1,605° F.); cover coats all fired 8 minutes at 800° C. (1,470° F.).

firing range were given poorer grades. However, in the heat of L_2 (No. 61), used for comparison with this series, no specimens were rated worse than grade 3, so the evidence was again inconclusive. Therefore, several further tests with additions of nickel, silicon, and aluminum were made. While no conclusive results were obtained in a limited number of experiments with ladle additions of one-half per cent and 2 per cent nickel, nor with 1 per cent aluminum, promising results were obtained with silicon additions made in the furnace. Table 13 and Figure 11 show that there was a noticeable improvement in the enameling properties of the blistering iron L_2 with a higher silicon content, addition of this element being made in the furnace. While the variation in silicon content was evidently not sufficient to cause a marked change in the average amount of combined carbon throughout the cross section of the castings, it is thought that this variation was large enough to affect the combined carbon in the surface layer. The phosphorus, as well as the silicon, contents of the strongly blistering iron, L_2, were increased in certain heats to correspond with the weakly blistering iron, R_2. Also a few tests were carried out using fused sodium carbonate as a fluxing addition, but the results of these experiments did not indicate any marked improvement.

TABLE 13.—*Tests of iron L_2 with and without additions of silicon (electric furnace melts)*

Plate No.	Iron	Approximate pouring temperature	Composition				Standard enamel ratings at firing periods shown in minutes							
			Carbon			Si[1]	3½	5	7½	10	12½	15	17½	Average
			Total	Graphite	Combined									
		°C.	*Per cent*	*Per cent*	*Per cent*	*Per cent*								
1-73	L_2	1,400	3.54 3.52	2.94 3.05	0.60 .47	2.35 2.30	2½	2	4	5	4	4	5	3.8
2-73	do	1,230					1	2½	4	5	5	4½	5	3.9
3-73	L_2+½ per cent Si	1,400	3.54 3.53	3.11 3.20	.43 .33	2.49 2.53	3	2½	3½	4	5	4	5	3.9
4-73	L_2+¾ per cent Si	1,400	3.41 3.49	3.01 3.01	.40 .48	2.64 2.65	3½	2	2	3½	4	5	3	3.3
5-73	L_2+1 per cent Si	1,400	3.48 3.48	2.99 3.03	.49 .45	2.91 2.93	2½	2½	2	3	3	3	4½	2.9
6-73	do	1,230					2½	2	2	3	3	3	4½	2.9

[1] The amounts of silicon found by analysis did not increase correspondingly with the amounts added, because a portion of the silicon was burned away.

4. SAND-BLASTING TESTS

A study was made of blistering and nonblistering irons as to the nature of the surface layer and its relation to blistering. First, it was necessary to find whether the irons varied in resistance to sand blasting. A regulated sand-blast tester for study of abrasion resistance was used. This consisted of a nozzle five-sixteenths inch inside diameter, through which a given amount of Ottawa silica sand or steel grit was passed at an air pressure of 80 pounds. The abrasive impinged on a 3 by 3 inch specimen placed 3½ inches from the nozzle, at an angle of 45° to the direction of the blast. The loss of weight of the specimen when blasted under these conditions was taken as a measure of the resistance to that type of abrasion.

Specimens of R_2 and L_2 as well as L_2, softened by adding nickel, were tested. As shown in Table 14, the average loss of weight was in the direction to be expected; that is, the blistering iron, L_2, lost less than the nonblistering iron, R_2, but the individual tests did not differentiate the irons sharply. Other factors than the combined carbon of the iron must come in, since L_2, plus nickel, with only 0.11 per cent combined carbon (see Table 12), was intermediate between L_2 without nickel and R_2. This method of testing produced sufficient abrasion to cut through the thin surface skin so that differences in hardness which might exist at the surfaces played only a small part in the final figure obtained. The test was repeated, by using successive portions of 600 ml (1,000 g) of sand and similarly

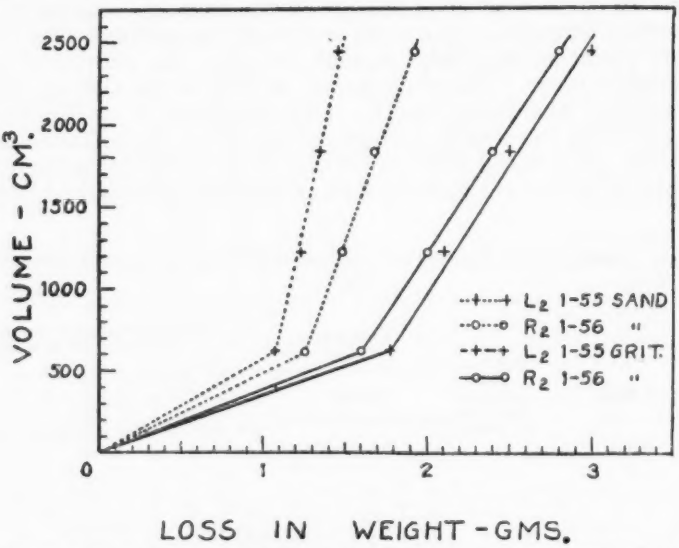


FIGURE 12.—*Loss in weight of different irons when blasted with different abrasives*

Curves show the relation between the volume of abrasive passed through the orifice of sand-blast apparatus and the loss in weight of specimens. The irons used were L_2, 1–55 and R_2, 1–56. The abrasives used were standard Ottawa silica sand and No. 14 steel grit.

with 600 ml (2,260 g) of steel grit as the abrasive on plates from different heats of irons L_2 and R_2. The results are plotted in Figure 12, and show that other heats of these irons fall in the same order as given in Table 14, when sand was used, but that the reverse was true when steel grit was used.

TABLE 14.—*Loss in weight during sand-blasting*

Heat No.	Iron	Specimen No.	Loss in weight	Average loss in weight
			g	*g*
2-56	R_2	1	1.2	1.6
		3	2.0	
2-55	L_2	5	.6	.8
		7	1.0	
57	L_2+0.5 per cent Ni	9	1.0	1.2
		11	1.4	

This test does not appear to offer promise as a means of distinguishing blistering from nonblistering iron. The surface layer is evidently too thin to allow satisfactory evaluation of its resistance to abrasion by this means.

5. STUDY OF BURNED-IN MOLDING SAND

There appeared to be a possibility that the condition responsible for blistering might be a layer of burned-in sand grains which had not been removed by sand-blasting, although it seemed likely that such material would be inert. Hence, specimens of nonblistering iron were deeply sand-blasted at one end and the amount of sand-blasting was decreased sharply toward the other end, where burned-in sand grains could be readily detected with a binocular microscope. These burned-in sand grains did not produce any blisters when the specimens were enameled.

In another test, molding sand was scattered over a deeply sand-blasted specimen and the enamel applied as usual. This specimen did not blister. Hence, adhering sand, in itself, does not appear to be a direct cause of blistering, though a burned-in layer would retard the removal of the outside layer of metal during sand-blasting.

Striking confirmatory evidence of this was obtained with a plate of blistering iron L_2 which had a firmly adhering scale of burned-in sand. This plate was sand-blasted while held at an angle to the sand stream so that one end was sand-blasted just enough to be visibly free from adhering sand, but not enough to remove this "microchilled layer." The blasting was progressively decreased as the other end was approached. A strip at the end was completely shielded from the blast. On enameling, the shielded strip was entirely free from blisters, although, of course, the adhesion of the enamel was not commercially satisfactory. The sand-blasted area showed progressively increasing blistering as the metal surface was more completely exposed. This test also gave conclusive evidence that blistering is due to a surface reaction and not to the freezing of "occluded" gas in the metal itself, since the portion which was not sand-blasted was as free to evolve such gas as that which was sand-blasted.

6. COMPOSITION OF SURFACE LAYERS

Since the surface layer involved is very thin and the surface of a casting is not perfectly smooth, any attempt to mill off the outside layer for chemical examination will result in contamination of it with underlying material. However, a comparison of the results of chemical analysis of the surface and of the body of the casting would appear to give useful indications. Heat 2–55 of iron L_2 with an average blistering index (Table 9) of 4.5—that is, badly blistering—and heat 3–56 of iron R_2 with an average index of 2.4 were compared. The data appear in Table 15.

TABLE 15.—*Chemical composition of surface layer and interior of cast plates of irons L_2 and R_2*

Elements	L_2 heat No. 2–55 (badly blistering)		R_2 heat No. 3–56 (weakly blistering)	
	Outside layer 0.003 inch thick	Comparison layer (0.01 inch thick) several hundredths inch beneath the surface	Outside layer 0.003 inch thick	Comparison layer (0.01 inch thick) several hundredths inch beneath the surface
Total C	2.71	3.54	2.84	3.31
Combined C	.45	.34	.42	.27
Graphitic C	2.26	3.20	2.42	3.04
Manganese	.61	.73	.45	.61
Phosphorus	.435	.500	.605	.835
Sulphur	.044	.037	.031	.022
Silicon	2.42	2.63	2.33	2.46
Nitrogen	.0033	<.0005	.0015	<.0005
Total	6.22	7.44	6.26	7.24
Iron by difference	93.78	92.56	93.74	92.76

It is seen that in both cases there is at the surface less total carbon manganese, phosphorus, and silicon, but more combined carbon and sulphur; that is, the surface skin seems to be higher in iron than the interior, which segregation is to be expected.

The increase in combined carbon appears especially significant, since that will obviously accompany the presence of a hard surface layer, which is difficult to remove by sand-blasting. There seems, therefore, to be a "microchilled" surface layer (micro refers here to the thickness of the chilled layer), which is apparently not necessarily controlled by the propensity of the iron to chill in the ordinary sense of giving a visibly thick layer of white iron on rapid cooling, and which may be different in its nature from an ordinary chilled layer.

7. MICROSCOPIC EXAMINATION OF "MICROCHILLED" LAYER

The difference in composition at the extreme surface is probably greater than is shown by the chemical analysis, since in machining off the surface layer, thin as it was, doubtless some material more nearly approaching the body of the casting in composition was included. The microstructure of the surface of iron R_2, heat 3–56 (fig. 13D), indicates it to contain much less combined carbon than the surface of iron L_2, heat 2–55 (fig. 14D). The surface of the best heat (4–55) of iron L_2 (fig. 15) appears to be more completely broken up into ferrite and graphite than is the case of heat 2–55.

8. EFFECT OF NITROGEN

The higher nitrogen content (Table 15) of the thin surface layer than that of the interior calls for attention, especially as the strongly blistering iron shows double the amount of nitrogen in the surface that the weakly blistering one does. The nitrogen might play a part in two different ways. If it is present as iron nitride, which decomposes at or below enameling temperatures (10), it constitutes a possible source of gas bubbles. If, on the other hand, it is present as chromium or titanium nitrides, these might decompose slightly at enameling temperatures, but the greater part of the nitrogen would

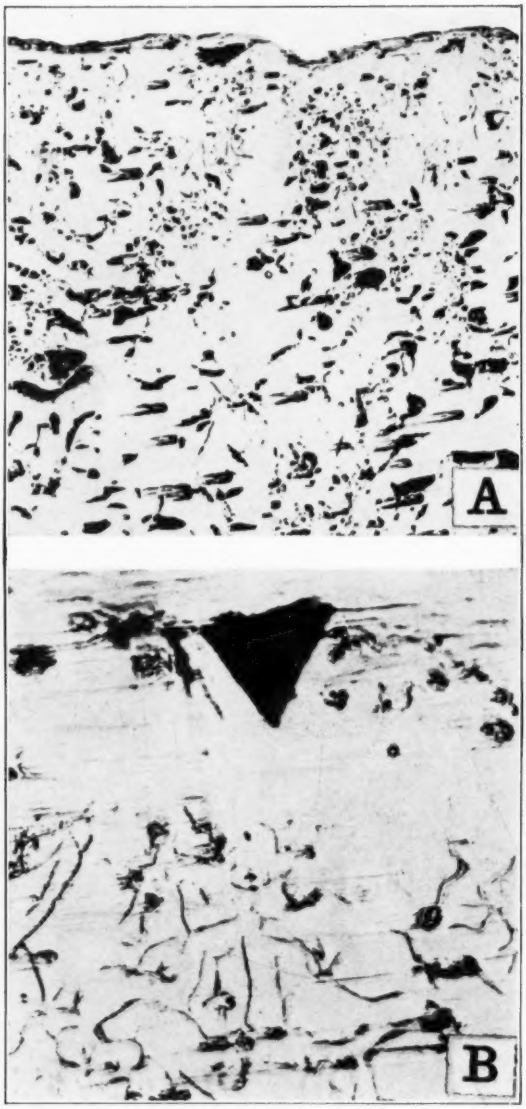


FIGURE 13.—*Cross section of surface layer. Iron R_2; heat 3–56*

Drag side, composition shown in Table 15. (Surface of specimens at top of these and all following micrographs. Specimens not enameled were nickel and copper plated before sectioning.) *A*, polished. × 100; *B*, polished. × 500.

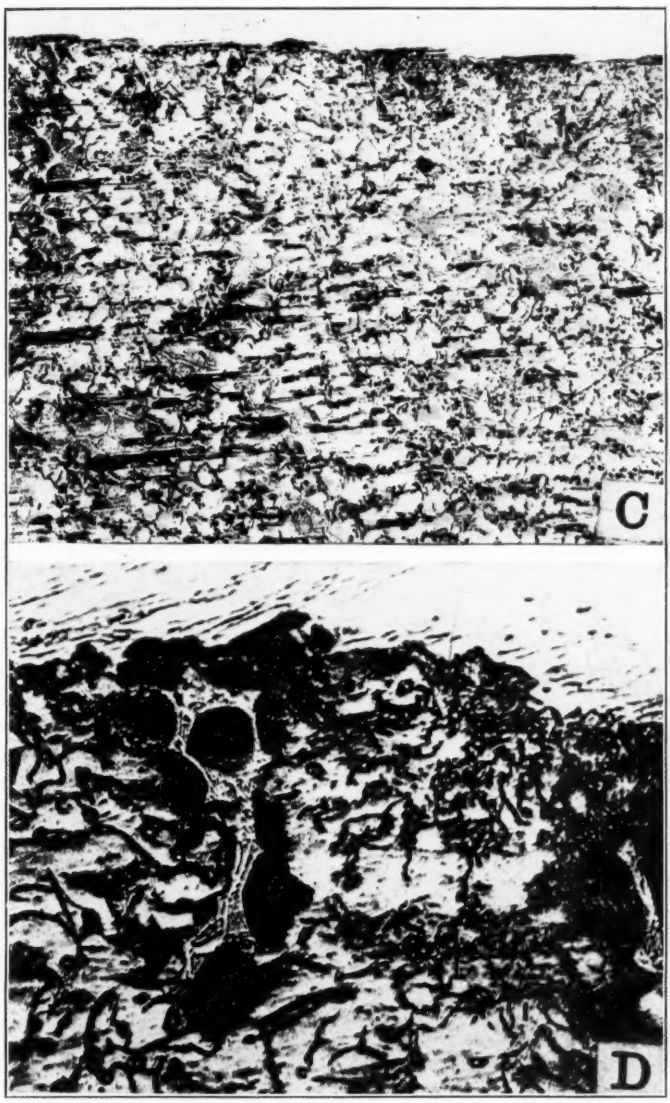


FIGURE 13.—*Cross section of surface layer. Iron R_2; heat 3–56*—Continued

C, etched in 5 per cent picric acid. × 100; *D*, etched in 5 per cent picric acid. × 500.

be retained and tend to form a hard skin as in the case of special steels containing aluminum and chromium, heated in an atmosphere of ammonia (11).

That nitrides probably play no direct part in the formation of blisters was indicated by the following test: Half of the drag side of strips 6 by ¾ by 3/16 inches of R_2 iron, heat 3–56, were lightly machined and both drag and cope sides were given the standard sand-blasting. These strips then were heated to 500° C (930° F.) in a stream of ammonia for periods of 1, 2, and 5 hours according to the usual method employed in forming nitride coatings. The nitrided strips were then very lightly sand-blasted and the cope side of each strip machined off to give a sample for chemical analyses for nitrogen, the layer removed being 0.003 inch thick. Analysis showed the nitrogen content of the surface layer of the three to be 0.05, 0.08, and 1.0 per cent, respectively. On enameling these specimens on the drag side, in the usual fashion, there was no sign of blisters either on the machined area or on the nonmachined area though both contained nitrogen in far higher proportions than that found on the surface layer of the blistering iron.

That it is comparatively easy to produce a nitride skin on ordinary cast iron is probably not well known. Osterman (11), however, has mentioned the commercial nitriding of cast iron for water pumps. Wheeler (11) found that washed metal (almost pure iron-carbon alloy of 3.65 per cent carbon) was hardly affected on heating in ammonia gas while a white cast iron of 2.15 per cent carbon, 0.33 per cent silicon, 0.12 per cent manganese, 0.20 per cent phosphorus, 0.21 per cent sulphur, readily formed a nonadherent surface layer containing almost pure iron nitride, beneath which the metal was somewhat decarburized.

There is some evidence that the minute amount of nitrogen introduced in melting steel, and presumably in cast iron, may be more stable than the nitride formed on the surface by heating in ammonia gas, and, hence, might decompose at a different temperature, perhaps just a temperature at which the gas would be caught in the enamel, so the test may not entirely exclude the possibility that nitrogen causes blistering.

9. SPECTROSCOPIC EXAMINATION

There is a possibility that traces of elements that would form hard nitrides might play a part in the formation of a hard skin. Spectroscopic analysis of the strongly blistering iron, L_1, and the weakly blistering iron, R_1, made early in the investigation, showed nickel to be absent, but titanium, vanadium, chromium, traces of aluminum, and, of course, copper to be present in addition to the elements usually reported in chemical analysis of cast iron. Chemical analysis for these elements and for total oxygen and hydrogen gave the results shown in Table 16.

TABLE 16.—*Content of elements not ordinarily determined in cast iron*

Designation of irons	Character	Cu	Ti	Cr	V	Al	O	H
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
L_1	Strongly blistering	0.07	0.08	0.025	0.030	(1)	0.002	0.0007
R_1	Weakly blistering	.03	.15	.010	.025	(1)	.004	.0005

[1] Less than 0.005 per cent.

Since copper is present in all pig iron and is not a carbide or nitride forming element, it can hardly be suspected of having anything to do with blistering. Vanadium and aluminum are essentially identical in the two irons. Titanium, a nitride-forming element, might be suspected, but the fact that the strongly blistering iron contains only half as much as the weakly blistering one seems to remove titanium from suspicion.

Gilmore (12) points out that aluminum and titanium act like silicon in favoring the softening of iron by the precipitation of graphite, and states that both vanadium and chromium assist carbon in remaining in the combined form, one-quarter of 1 per cent of chromium holding 0.80 per cent carbon in the combined form after a malleableizing anneal.

10. EFFECT OF CHROMIUM

Chromium was present in the strongly blistering iron, L_1, in appreciably larger amount than in the weakly blistering, R_1.

Since small amounts of chromium are known to increase the chill on cast iron (13, 14) and to interfere considerably with the malleableizing anneal of malleable cast iron, by tending to retain the carbon in the combined form, there is a possibility that even this slight difference in chromium content might favor the formation or retention of a surface layer higher in combined carbon, hence, harder and more difficult to remove in sand blasting.

To examine further the hypothesis that the chromium content might have a connection with the propensity toward blistering, the irons used in the latter part of the investigation were analyzed for chromium, with the results shown in Table 17.

TABLE 17.—*Enamel ratings of irons with different chromium contents*

Iron	Heat No.	Chromium	Enamel rating (Table 9)
		Per cent	
L_2	1–55	0.04	4.8
L_2	4–55	.04	3.1
R_2	4–56	.04	3.7
R_2	2–56	.03	2.4
Southern charcoal	42	.03	(1)
Southern	41	.10	(1)

[1] Ratings not comparable, since irons were tested only at the bureau.

It will be noted that the strongly blistering iron, L_2, and the worse heat (4–56) of the weekly blistering iron, R_2, contain slightly more chromium than the better heat (2–56) of R_2. While the difference is very slight, it is in the direction of damage due to chromium.

Although the enamel rating obtained with southern iron is not comparable to the other ratings, there is little doubt that it has as little blistering tendency as any iron studied. Yet it contains much more chromium than any of the others, so that the mere presence of chromium can not be taken as the sole cause for blistering. This can not be regarded as entirely eliminating chromium from consideration, because the formation of the microchilled layer is very evidently a matter of delicate balance and the effect of chromium in irons of different composition as to other elements may not be the same.

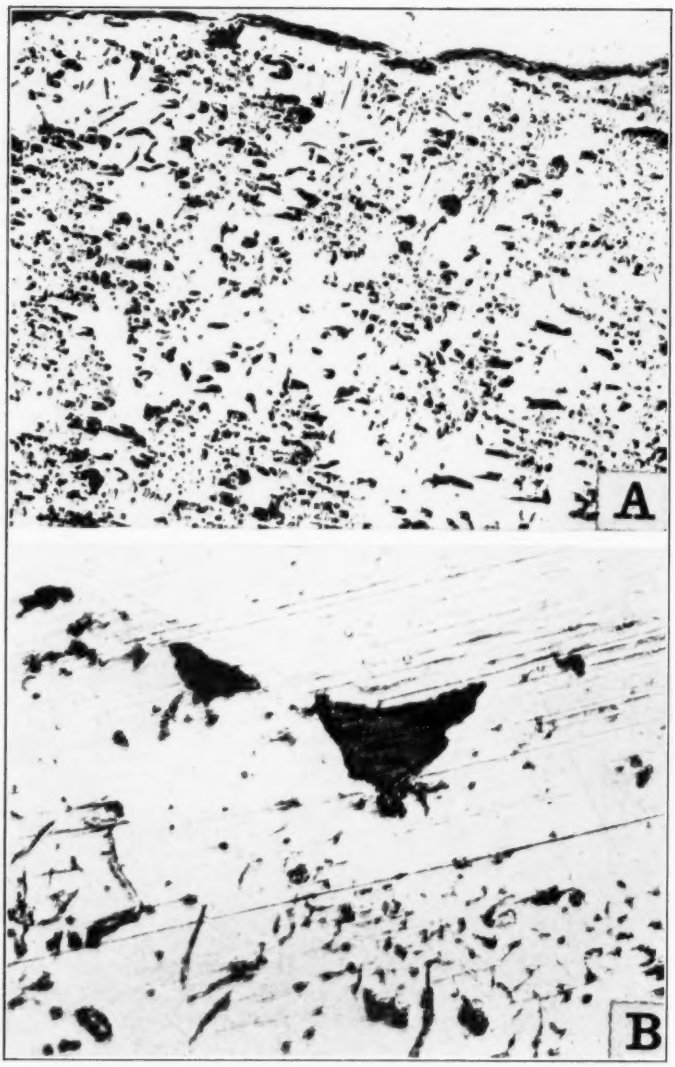


FIGURE 14.—*Cross section of surface layer. Iron L_2; heat 2–55*

Drag side, composition shown in Table 15. *A*, polished. × 100; *B*, polished. × 500.

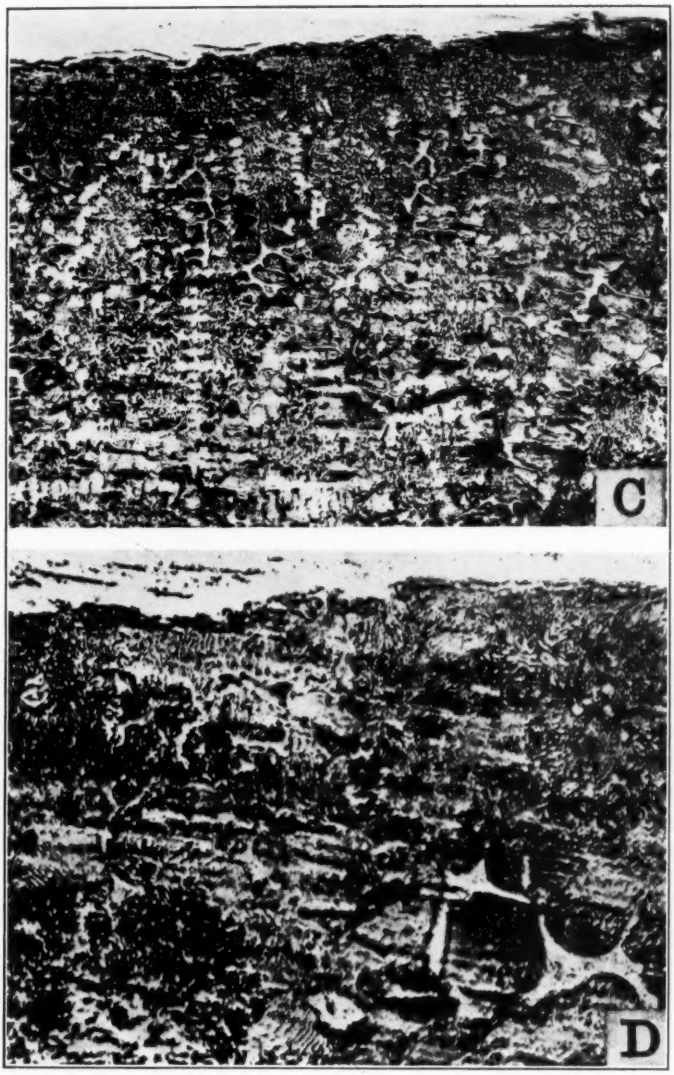


FIGURE 14.—*Cross section of surface layer. Iron L_2; heat 2–55*—Continued

C, etched in 5 per cent picric acid. × 100; *D*, etched in 5 per cent picric acid. × 500.

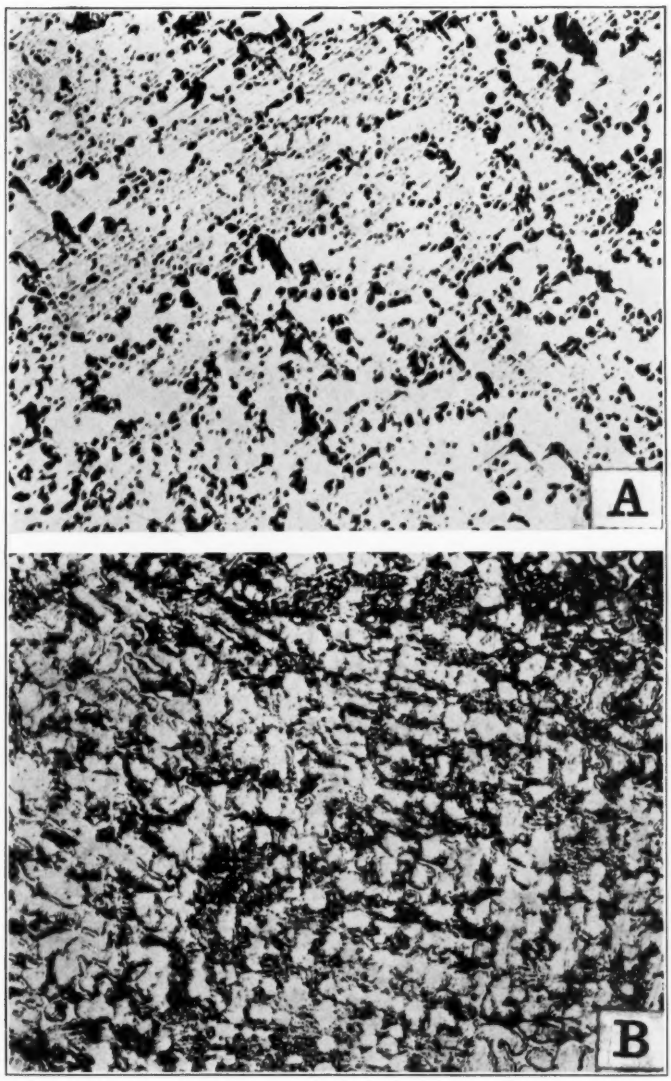


FIGURE 15.—*Cross section of surface layer. Iron L_2; heat 4–55*

Drag side; this heat was less strongly blistering than the companion heats (1–55, 2–55, and 3–55) of iron L_2. *A*, polished. × 100; *B*, etched in picric acid. × 100.

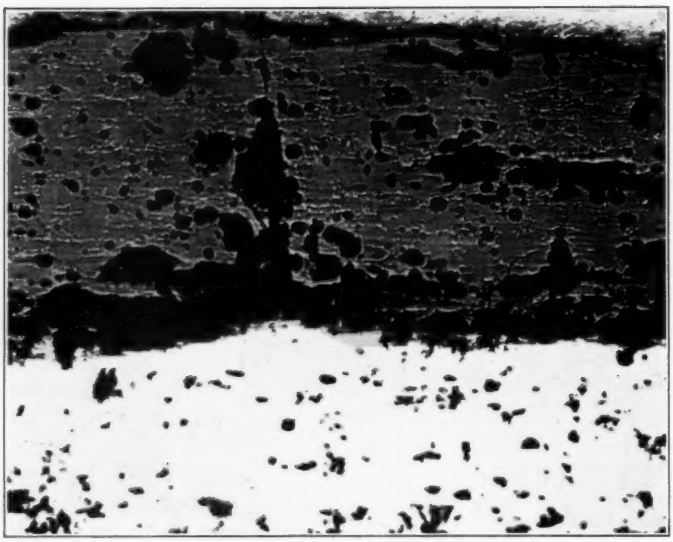


FIGURE 16.—*Cross section of enamel and surface layer of iron. Southern iron; heat 41*

Polished. × 100. Note interconnected channels in the enamel. No blisters were observed on this specimen. Ground coat fired 10 minutes at 875° C. (1,605° F.) and cover coat 8 minutes at 800° C. (1,470° F.).

In order to study the chromium problem more thoroughly, an experiment was made to see whether addition of chromium to the weakly blistering northern iron, R_2, increased its propensity to blister. As may be seen from Table 18, a noticeable increase in blistering accompanied the addition of 0.03 per cent chromium, but the larger additions (0.05 per cent and 0.10 per cent) showed no effect.

TABLE 18.—*Enameling tests of irons R_2 and L_2 without and with additions of chromium (electric furnace melts)*

Plate No.	Irons	Approximate pouring temperature	Standard enamel ratings at firing time shown in minutes							
			3½	5	7½	10	12½	15	17½	Average
		°C.								
1–71	R_2	1,400	4	1	2	2	3	2	2½	2.4
2–71	R_2+0.03 per cent Cr	1,400	4	2½	4	3	3	4	2½	3.3
3–71	R_2+0.05 per cent Cr	1,400	4	1	1	2	2½	3	3	2.4
4–71	R_2+0.1 per cent Cr	1,400	3½	1	2	2	3	2½	3	2.4
5–71	R_2	1,390	3	2	3	2	3	3	3	2.7
6–71	do	1,250	4	2½	2	3½	3½	2½	2	2.9
1–72	L_2	1,400	2½	2½	2½	5	5	5	5	4.0
2–72	L_2+0.03 per cent Cr	1,400	3	2½	2½	5	5	5	5	4.0
3–72	L_2+0.05 per cent Cr	1,400	3	2½	2½	4	5	5	5	3.9
4–72	L_2+0.1 per cent Cr	1,400	3	2½	2	5	5	5	5	4.0
5–72	L_2 tapped from furnace 14 minutes after 1–72 was tapped	1,400	2½	2	2½	5	5	5	5	3.9
6–72	L_2 tapped from furnace 20 minutes after tapping of 5–72	1,320	3½	2½	5	4½	4½	5	5	4.3

Similar experiments were carried out with additions of chromium on the blistering iron L_2 with the purpose of stabilizing combined carbon in the surface layer of those castings. As is shown in Table 18 and Figure 11½, chromium, in the quantities used, had practically no effect.

VII. ERRATIC BEHAVIOR OF PIG IRON

The erratic behavior of iron containing small amounts of chromium, commented on above, reminds one that many cases are known in which inexplicable differences are found in the behavior of different lots or heats of cast iron that do not differ materially in composition as determined by ordinary chemical analysis (15, 16, 17). Sometimes this can be explained on the basis of a delicate balance among elements (18, 19).

Piwowarsky (18) finds that the combined carbon content of gray iron castings is affected by the temperature and duration of superheating of the melt. These factors also produce variations in the number and size of graphite nuclei upon which graphite will be precipitated on freezing.

VIII. STUDY OF GASES AND GAS-FORMING ELEMENTS

1. OXYGEN

In work by Herty and Gaines (29), of the Bureau of Mines, it has been found that pig iron tapped after a blast furnace "slip" may contain an excessive amount of suspended silica or silicates in a very fine state of subdivision, and that these, being difficult to reduce or flux out in steel making, give inferior steel.

It does not, however, appear likely that the presence or absence of such inclusions is directly responsible for the difference between blistering and nonblistering irons. If the suspended particles are not reduced by the carbon of the iron while it is molten, it is not likely that they will be reduced by it in the solid metal when heated only to enameling temperatures. Hence, the evolution of CO from within the metal itself by reaction of inclusions during enameling is not a plausible explanation for blisters. Moreover, the vacuum-fusion method for total oxygen determines the oxygen of silica and silicates, hence will reflect the amount of inclusions present. As shown in Table 16, however, very little difference was found in the oxygen content of the two irons, the blistering iron containing even slightly less oxygen than the nonblistering one.

2. HYDROGEN

The difference in the hydrogen content of the two irons is within the precision of the analytical method, and since the amounts are so nearly the same, no indication is given that hydrogen is a factor.

3. SULPHUR

There is also a possibility that the gas might come from the oxidation of manganese sulphide or iron sulphide at the surface of the metal. To examine this hypothesis, sulphur determinations were made on the surface layer (0.003 inch thick) milled off of specimens of the strongly blistering iron, L_2, heat 2–55, after the usual sand blasting, and of other specimens of the same heat that had been put through the heating cycles of the enameling process under oxidizing conditions but without enamel. These cycles consisted of heating in air 12½ minutes at 875° C. (1,605° F.), cooling in air and again heating in air 8 minutes at 800° C. (1,470° F.). The amount of sulphur was not changed, being 0.050 per cent in each case, and this indicated that there is no preferential oxidation of sulphur and that the blister forming gas is probably not SO_2.

4. GAS IN BLISTERS

If the composition of the gas in the blisters could be determined, one would have a very useful clue as to their source. On piercing the blisters of an enameled specimen under water, collecting and analyzing the gas, it was found to be air. Microscopic examination of the cross sections of enamel coatings (fig. 16) indicated that many of the internal bubbles were connected by channels with each other and frequently with the air, so that whatever the original gas they contained during the process of blistering, it may escape and be replaced by air. Hence, it was necessary to collect the gas formed in the act of blistering.

First of all a determination of whether the enamel alone and the iron alone evolve gas on heating was necessary.

That gas is evolved from the enamel alone is shown by the fact that the ground and cover coats used in the standard enameling procedure (including the clay used) dried as in the enameling process, exposed to the air for 42 hours, dried again at 100° C. for 1 hour and finally heated to 500° C. for 12 minutes, lost weight as follows:

	Total loss in weight up to—	
	100° C.	500° C.
	Per cent	*Per cent*
Ground coat	0.53	2.24
Cover coat	.07	.62

Presumably the greater part of the loss at 500° C. (930° F.) represents water of constitution of the clay, or at least firmly adsorbed moisture.

The ground coat and the clay used in it were then tested at enameling temperatures. The ground coat slip (containing 15 per cent clay on a dry basis) after first drying for an hour at 130° to 140° C. (265° to 285° F.) followed by heating at 830° C. (1,525° F.) for eight minutes, gave off 0.10 per cent of CO_2. The clay alone gave off, beside an undetermined amount of moisture, 0.43 per cent CO_2. Good agreement in both figures was obtained in duplicate determinations. Hence, the ground coat slip gives off 0.06 per cent CO_2 due to the clay and 0.04 per cent CO_2 due to the frit itself. This amount of oxidized carbon, however, is of little importance as compared with amounts of similar gases from other sources, as will be shown later.

5. GAS AND IRON ALONE HEATED IN NITROGEN

There were then selected for the subsequent tests, specimens of iron varying in their tendency toward blistering, as follows:

Iron	Heat	Average blistering index [1]
L_2	1-55	4.8
L_2	2-55	4.5
L_2	4-55	3.1
R_2	2-56	2.4
Southern	41	(1.8)

[1] See Table 9.

The average rating (1.8) of southern iron, heat 41 (poured at 1,400° C. (2,550° F.)) was obtained from tests made at the bureau only, hence, is not comparable with other averages which include results obtained in several laboratories. The first four specimens are northern irons. It is to be noted that iron L_2, 4–55, is much less blistering than the other heats of L_2–55.

The total surface area of each sample (both sides and all edges) was about 5 square inches, and each weighed about 50 g. These samples were sand-blasted in a manner corresponding to the usual method of preparation for enameling, placed in a furnace through which the desired gas was passing, and heated. Any CO_2 and CO formed were collected in an analytical train and determined gravimetrically. In the first series, after drying for an hour at 150° C. (300° F.), the specimens were heated for 15 minutes in a stream of oxygen-free nitrogen at 875° C. (1,605° F.). The results are given in Table 19.

TABLE 19.—*Weight of evolved gases from iron specimens heated in oxygen-free nitrogen*

Iron	Heat	Weight in grams of evolved gases per specimen			
		CO_2	CO	H_2	CO_2 equivalent of total oxidized carbon
L_2	1–55	0.0040	0.0032	Nil.	0.009
L_2	2–55	.0023	.0029	Nil.	.007
L_2	4–55	.0029	.0035	Nil.	.008
R_2	2–56	.0032	.0035	0.0001	.009
Southern	41	.0058	.0056	.0001	.015
		.0024	.0022		
		.0055	.0062		

Although the nitrogen was treated to remove the bulk of any oxygen present, the specimens after heating were darkened slightly, southern iron 41 being the darkest. The uniformity of the amount of equivalent CO_2 from the L_2 and R_2 specimens indicates that the test does not differentiate between strongly and weakly blistering irons, and probably reflected merely the amount of air adsorbed on the metal surface or that entering the nitrogen-filled tube when the specimen is inserted, or possible traces of oxygen remaining in the nitrogen.

6. GAS FROM IRON ALONE HEATED IN AIR

In the next series of tests the specimens were heated in CO_2-free air instead of in nitrogen. The specimens dried as before, were heated for 15 minutes at 875° C. (1,605° F.). While the carbon of the cast iron may burn to CO at the surface, the CO will, under the test conditions, be burned almost entirely to CO_2, only traces of CO being collected in the analytical train. These traces were calculated as the equivalent CO_2. The complete results are given in Table 20.

TABLE 20.—*Weight of total CO_2 and H_2 evolved from iron specimens heated in CO_2-free air*

Iron	Heat	CO_2 equivalent of total oxidized carbon	Weight H_2
		g	*g*
L_2	1–55	0.022	0.0001
L_2	2–55	.013	.0001
L_2	4–55	.008	.0001
R_2	2–56	.010	.0001
Southern	41	.017	.0001

Under the above conditions of heating, the most strongly blistering castings produced the most CO_2, although the weakly blistering southern iron produced nearly as large an amount of CO_2 as one of the strongly blistering irons. The appearance of the oxidized surface, however, did show a consistent relation to the blistering tendency. The specimens of the 1–55 and 2–55 heats of iron L_2 had a decidedly rough surface. Heat 4–55 of L_2, which was a good example of weakly blistering iron, was decidedly smoother and had the same appearance as the specimen of iron R_2 heat 2–56. The southern iron was still smoother, having a velvety appearance. In neither of the above two series of tests was there a certainly detectable amount of hydrogen evolved.

7. GAS FROM ENAMEL-COATED IRONS HEATED IN NITROGEN

In a third series of gas-evolution tests, the iron specimens were coated on all sides with the standard ground coat, about 0.9 g of wet ground coat being applied. The specimens were dried at 80° to 90° C. for 40 minutes. They were then inserted into the hot furnace tube through which oxygen-free nitrogen was passing, and heated at 875° C. (1,605° F.) for 20 minutes. The firing time was longer than in the regular enameling tests because of the smaller heat capacity of the furnace as compared with furnaces for regular enameling. Specimens coated on one side only and fired for a shorter period in preliminary tests had the appearance of being underfired.

Since the ground coat contained clay with water of constitution, the gas passing from the tube was scrubbed free from water vapor by a drying tower. The equivalent of the total oxidized carbon evolved is shown in Table 21. All figures are averages of two closely agreeing determinations.

TABLE 21.—*Gas evolved from cast-iron specimens coated with ground enamel and heated in nitrogen*

Iron	Heat	CO_2 equivalent of total oxidized carbon [1]	Weight H_2
		g	g
L_2	1–55	0.008	Nil.
L_2	2–55	.008	Nil.
L_2	4–55	.006	Nil.
R_2	2–56	.006	Nil.
Southern	41	.007	0.0001

[1] Of this CO_2 only 0.0005 g was in all cases due to the ground coat alone.

It would be assumed that much of the air adsorbed on the surface of the iron specimens before spraying with ground coat would be displaced by the water of the ground coat, but the dry ground coat would presumably adsorb air. It is not possible, therefore, to tell whether the oxygen of the CO_2 comes from adsorbed air, air admitted in inserting the specimens into the tube, or from oxidation of the lead oxide of the ground coat. By comparing the four heats of northern irons it might appear that the more strongly blistering ones have the carbon at their surfaces in more readily oxidizable form, but the southern iron is out of line with this explanation.

The surface appearance of the specimens was again very characteristic, each pair of duplicate specimens agreeing closely in appearance. The specimens of iron L_2 heats 1–55 and 2–55 (the most strongly blistering ones) had the ground coat in very rough, pebbly form. Heats L_2, 4–55 and R_2, 2–56 (weakly blistering) had the coat in less rough form, while the weakly blistering southern iron was very smoothly and evenly coated. The machined edges of all the specimens were smoothly and uniformly coated with a glossy coat. The appearance of the specimens is shown in Figure 17. The difference in surface roughness is more likely an effect of some condition leading to blistering rather than the cause, since it will be recalled that removing the surface of "blistering" iron by pickling was as efficacious as machining, though the pickled surface was extremely rough and the machined surface smooth.

8. GAS FROM IRON AND ENAMEL HEATED IN AIR

In the fourth series of gas evolution tests the iron specimens, coated with ground coat enamel and dried as in the preceding series, were heated in CO_2-free air for 20 minutes at 875° C. (1,605° F.). The CO_2 equivalents of the total oxidized carbon in this series were less for all the irons than in the series of uncoated irons heated in air but remained in the same relative order as in the earlier series in air. (See Table 22.)

TABLE 22.—*Gas evolved from cast-iron specimens coated with ground enamel and heated in air*

Iron	Heat	CO_2 equivalent of total oxidized carbon	Weight H_2
		g	*g*
L_2	1-55	0.012	0.0001
L_3	2-55	.011	.0001
L_4	4-55	.009	Nil.
R_2	2-56	.010	Nil.
Southern	41	.011	Nil.

The specimens from the series given in Table 22 were then coated with the standard cover coat enamel in amounts equivalent to 23 g per 18 square inches of surface, dried, and then heated as before in the tube furnace. This heating was for 12 minutes at 800° C. (1,470° F.). Very small amounts of oxidized carbon were evolved during this heating and in quite the same amounts from all specimens as shown in Table 23.

TABLE 23.—*Gas evolved in firing cover coat*

Iron	Heat	CO_2 equivalent of total oxidized carbon
		g
L_2	1-55	0.003
L_3	2-55	.004
L_4	4-55	.004
R_2	2-56	.005
Southern	41	.004

9. RATE OF CARBON OXIDATION

The data obtained in all of the preceding tests indicate that carbon oxidized from the surface of the iron specimens is the chief source of the gas evolved during the firing of ground-coat enamels of cast iron. There is little or no evidence that either moisture or the oxide constituents of the enamel take an appreciable part in this oxidation of carbon from the surface of the iron. Oxygen of the air present in the enameling furnace appears to be the oxidizing agent.

The foregoing experiments on gas evolution have referred only to the total amount of gas evolved during the firing period. It is apparent, however, that any rapid and large evolution of gas from a specimen in the early stages of burning on an enamel coat should have very little effect in forming blisters in the enamel. It is only after the enamel coat has been fused over and completely covers the surface of the iron that gas evolution will cause blisters. More probably, only the gas evolution which continues well toward the close of the firing period produces blisters which are not healed by the fused enamel.

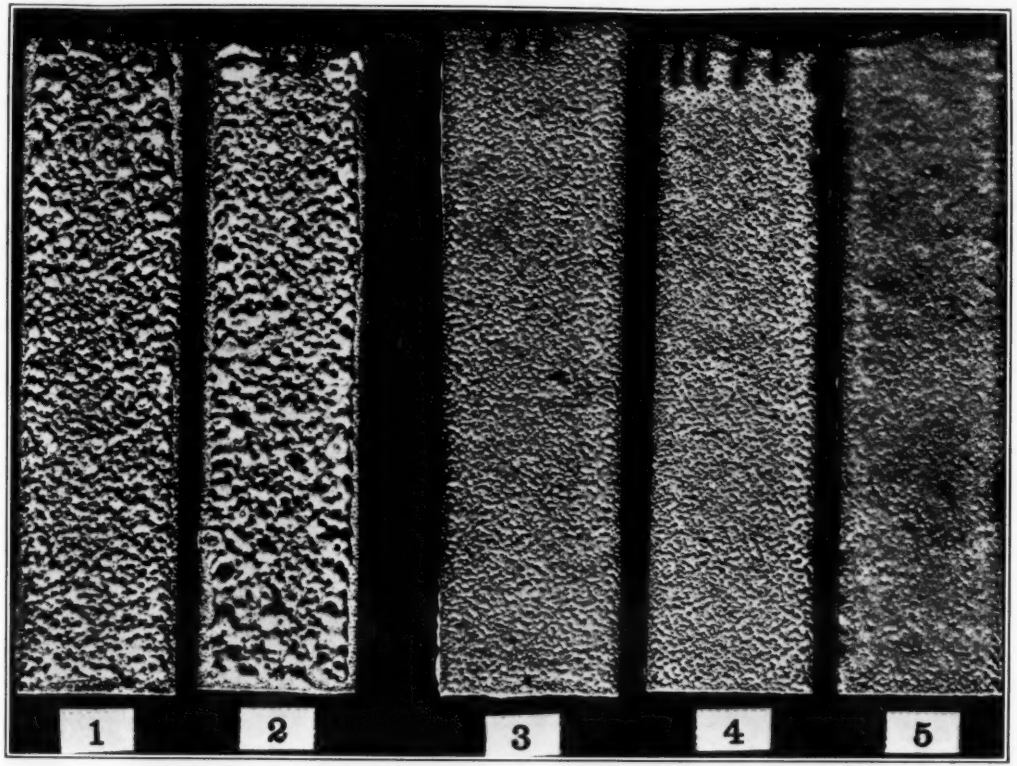


FIGURE 17.—*Surface appearance of specimens of strongly blistering and weakly blistering irons after firing the ground coats 20 minutes in nitrogen*

No. 1, iron L_2, heat 1–55, strongly blistering; No. 2, iron L_2, heat 2–55, strongly blistering; No. 3, iron L_2, heat 4–55, weakly blistering; No. 4, iron R_2, heat 2–56, weakly blistering; No. 5, Southern iron, heat 41, weakly blistering.

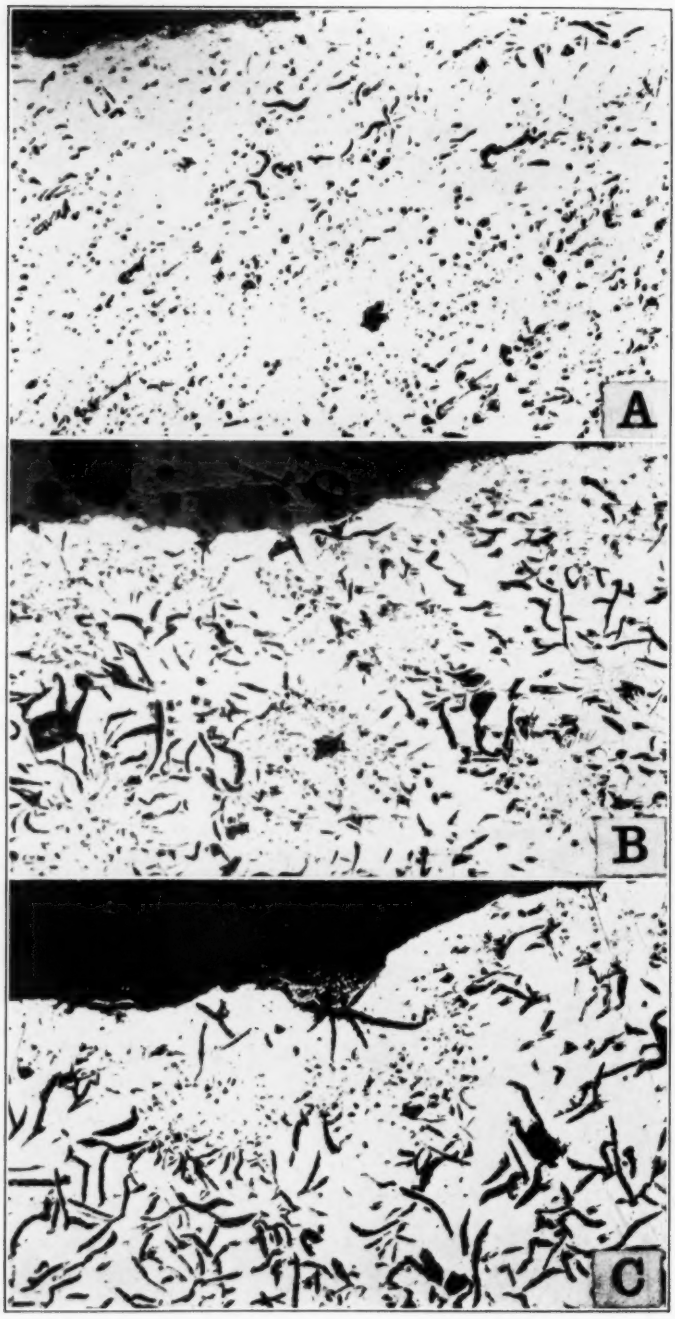


FIGURE 19.—*Illustrating agglomeration of graphite particles upon enameling. Iron R_2; heat 43*

Polished. × 100. *A*, drag side edge of cross section before enameling; *B*, specimen enameled: Ground coat fired 3 minutes at 875° C. (1,605° F.); cover coat 8 minutes at 800° C. (1,470° F.). No blisters were observed; *C*, specimen enameled: Ground coat fired 10 minutes at 875° C. (1,605° F.); cover coat 8 minutes at 800° C. (1,470° F.). No blisters were observed.

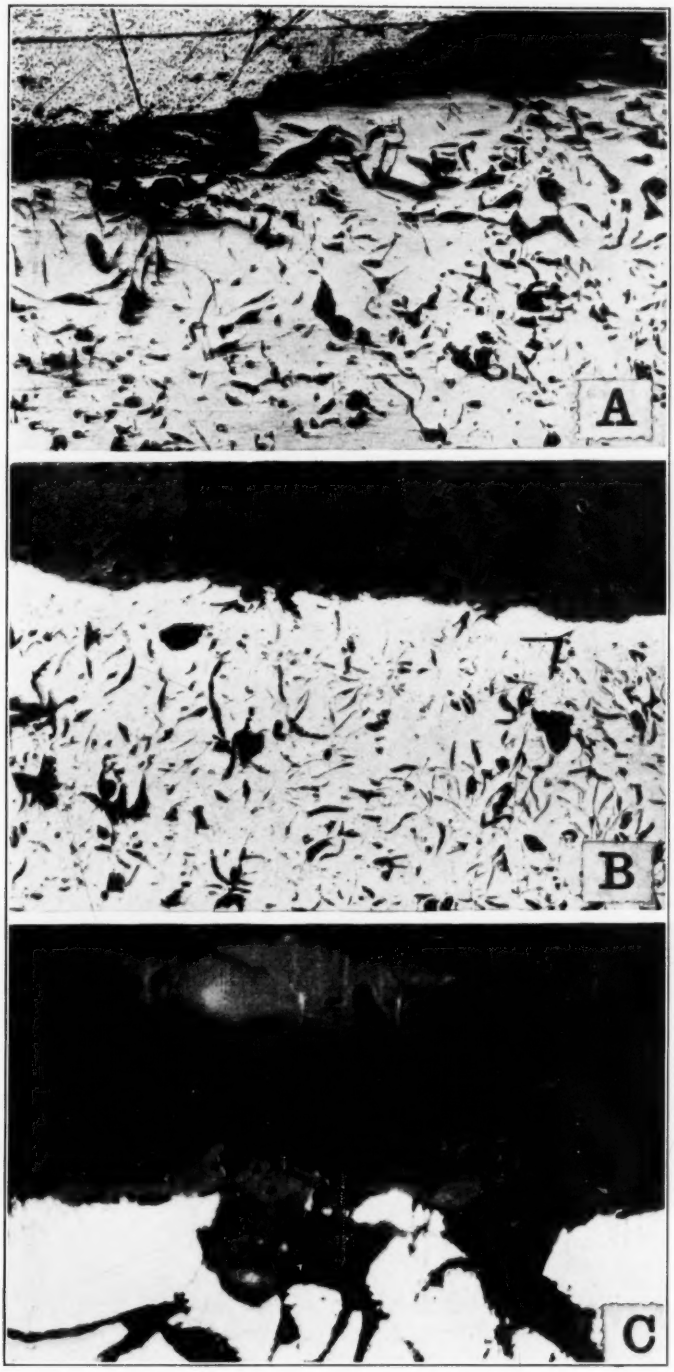


FIGURE 20.—*Cross section of surface of blistering iron, before and after enameling. Iron L_2; heat 50*

A, polished. × 100. Drag side of cross section before enameling; *B*, polished. × 100; *C*, polished. × 500; specimen thickly blistered. Ground coat fired 10 minutes at 875° C. (1,605° F.); cover coat 8 minutes at 800° C. (1,470° F.).

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In order to throw light on the relative rates of gas evolution (that is, carbon oxidation) from irons at the various stages of the enamel firing period, the following experiment was made: Strips of the typical strongly blistering iron, 1–55, and of the three weakly blistering irons, 2–56, 4–55, and southern 41, were cleaned by the usual sand-blast procedure, sprayed with the standard ground-coat enamel,

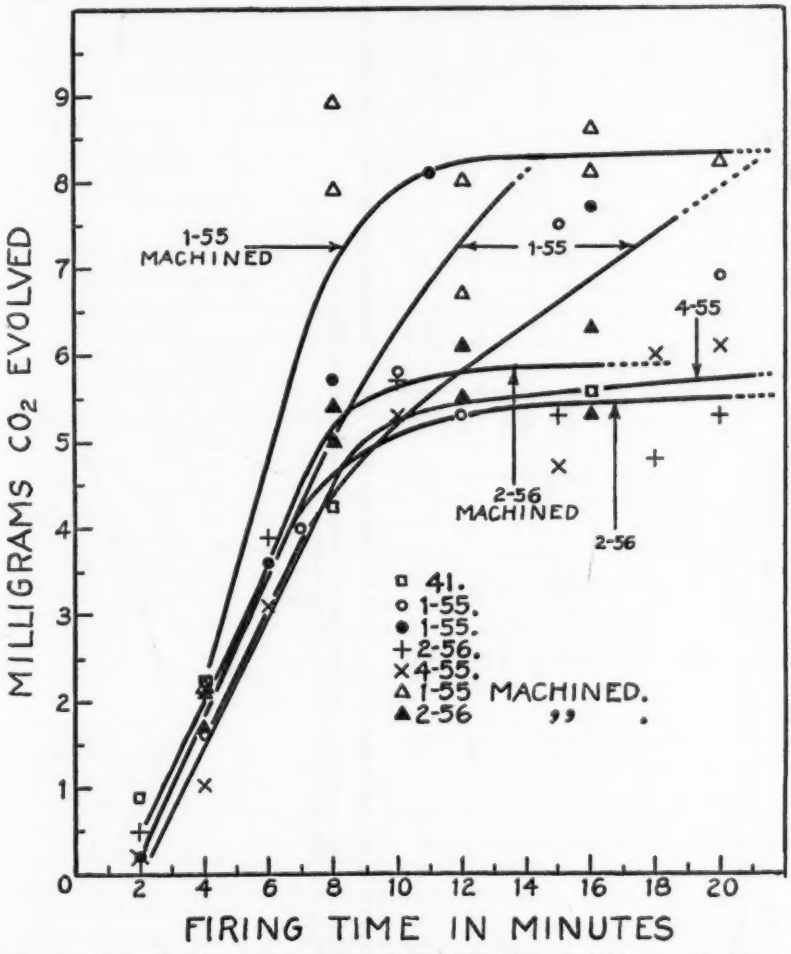

FIGURE 18.—*Weight of evolved $CO+CO_2$ (calculated to CO_2) plotted against firing periods*

All specimens completely coated with ground coat and fired at 875° C. (1,605° F.) in CO_2-free atmosphere. Each point represents one specimen and the corresponding analytical determination. L_2, 1–55, is a strongly blistering type of iron, while all of the others (including L_2, 1–55, machined) are weakly blistering ones.

dried and fired for varying periods of time up to a total of 20 minutes. The evolved oxides of carbon were determined in the manner previously described. The results are given in Table 24 and in Figure 18.

From this figure, it is evident that the amount of carbon oxidized and the rate of oxidation were nearly the same for all the weakly blistering irons and for the two series of tests with L_2, 1–55 (the strongly blistering iron) up to a firing time of about 8 to 10 minutes.

TABLE 24.—*Relative rate of oxidation of carbon from cast irons during enameling*

[Irons cleaned in sand blast, sprayed on both sides with standard ground coat, dried, and heated at 875° C. in CO_2-free air for the periods indicated]

Designation of irons	Heat No.	Character	Time of heating (in minutes)											
			2	4	6	7	8	10	11	12	15	16	18	20
			Evolution of CO_2 (in g)											
L_2	1–55	Blistering	[1] (0.0002) [2] .0002		(0.0041) .0035		(0.0065) .0056		(0.0092) .0079			(0.0087) .0075		
L_2	1–55	do		0.0016		0.0040		0.0058		0.0053	0.0075			0.0069
L_2 (machined)[3]	1–55	do					.0079			.0067		.0086		.0082
Do.[3]	1–55	do		.0022			.0089			.0080		.0081		
R_2	2–56	Weakly blistering	.0005	.0016	.0039			.0057			.0053		0.0048	.0053
R_2 (machined)[3]	2–56	do		.0017			.0050			.0061		.0063		
Do.[3]	2–56	do		.0021			.0054			.0055		.0053		
L_2	4–55	do	.0002	.0010	.0031			.0053			.0047		.0060	.0061
Southern	41	do	.0008	.0023			.0043					.0056		

[1] The first set of specimens of 1-55 were ⅞ inch wide instead of ¾ inch as in all other sets of this table. The values in parentheses are the actual values given by the ⅞ inch specimen.

[2] These values are calculated for a ¾-inch wide specimen from the data given by the above ⅞-inch wide specimen.

[3] These samples were machined down 0.003 inch on both sides, then treated as others.

At the 8 to 10 minute firing period, however, the rate of carbon oxidation fell off very noticeably with all three [3] of the weakly blistering irons and there was almost no evolution of gas (oxidized carbon) from these irons from 10 or 12 minutes to the 20-minute limit of the firing periods of this test. Gas evolution practically ceased over that portion of the enamel firing period during which it would naturally be expected to cause blistering.

Of course, the whole cycle might be completed in a much shorter time in a furnace of greater heat capacity. Furthermore, it should be borne in mind that the first part of this period corresponds approximately to firing the ground coat, and the latter part to the additional heating that is necessary in firing the cover coat. It is during the latter part of this second period that it is important for gas evolution to be kept at a minimum. The two curves for the duplicate experiments with iron L_2, 1–55, the badly blistering iron, show no decrease in rate of carbon oxidation at the point where the curves for the weakly blistering irons flatten out, but indicate a continuing evolution of oxidized carbon practically to the end of the firing period used. Whether or not the curves flatten out here is not certain in the absence of additional points beyond the 20-minute firing period. The question arose as to whether the curves, which flatten out at the 8 to 10 minute period, might begin to rise again if heating were continued, as, for instance, in the application of three or more coats of enamel. While the tests (fig. 18) were not carried beyond 20 minutes in any case, the fact that blisters seldom occur on reenameling castings, which may have blistered in the first enameling, seems to indicate that such a secondary rise in the gas-evolution curve, if it does take place, does not begin soon enough to give trouble in practical enameling.

The above data on the rate of carbon oxidation from the surface of enamel-coated cast-iron specimens all relate to iron cleaned by the normal sand-blast procedure. It will be recalled that machining a 0.003-inch layer from the surface of a strongly blistering iron strikingly reduced the tendency to blister.

If the cessation of oxidation of carbon relatively early in the firing period is the controlling characteristic of nonblistering irons, as is indicated by the curves for sand-blast cleaned irons in Figure 18, then a blistering iron, from the surface of which a 0.003-inch layer has been machined, might be expected to behave similarly. Specimens of L_2, 1–55, and R_2, 2–56, were machined in this way, lightly sand-blasted, and then treated exactly as the regularly sand-blasted specimens of the same irons had been treated, to determine the rate of carbon oxidation. The data on CO_2 evolution from the machined specimens are given in Table 24 and are plotted in Figure 18.

These curves show that machining off the surface of iron R_2, 2–56, had no influence on the rate of carbon oxidation from its surface nor on the point at which oxidation of carbon ceases. Machining off the surface of L_2, 1–55, however, noticeably increased the rate of carbon oxidation during the first 8 minutes of the firing period, but at the 8 to 10 minute point the evolution of oxidized carbon practically ceased.

[3] A curve for southern iron 41 has not been drawn in Figure 18, since for that iron only one value for CO_2 evolution was obtained between the 4-minute and the 16-minute firing periods. The points for this iron are given in the figure and indicate that the curve for this iron would not differ greatly from those for the other weakly blistering irons.

10. CORRELATION OF GAS EVOLUTION DATA WITH PREVIOUS DATA

It was found possible to distinguish between strongly blistering and weakly blistering irons on the basis of the breadth of the range of firing periods within which enameling could be accomplished with relative freedom from blisters. If an iron has a sufficiently strong blistering tendency, this range will be so narrow that it is virtually nonexistent, as in the case of iron L_2, 1–55 (Table 9). An iron having a somewhat weaker blistering tendency, as L_2, 3–55, in the same table, gave much better results at 7½, and even at 10 minutes of firing the ground coat, than at the longer periods, while with iron R_2, 2–56, the range was so broad that the results were still moderately good at the 15 to 17½ minute periods. In all cases, however, the average results at 3 minutes were unsatisfactory. The question arises as to just how these facts fit in with the foregoing data on gas evolution.

In the first place, it is obvious that the amount of blistering will be controlled by the rate of gas evolution during that part of the firing process in which the cover coat is able to entrap the evolved gas; that is, after it has begun to fuse. With this fact in mind, it can be readily seen that when the firing period of the ground coat is very short, then (fig. 18) blisters should be expected to appear on even the best irons studied, since the cover coat will be fired while gas is still being evolved just as rapidly as from a strongly blistering iron.

In the case of the specimens which are fired longer, there are three factors to take into consideration. One is, of course, the steepness of the gas-evolution curve during the critical period; another is the degree of permeability of the ground coat, which increases as the firing period increases, and the third is the time-lag factor which influences the actual progress of the gas bubbles through the comparatively thick cover coat.

With any specific firing treatment, the number and character of blisters will depend upon the rate of gas evolution during the critical part of the firing period. An iron in which this rate is intermediate will give comparatively good results within a narrow range at the shorter firing periods because the comparative impermeability of the ground coat and the time necessary for the evolved gas to work its way through the cover coat combine to delay the actual appearance of blisters at the surface of the specimen. If the ground coat is fired longer on an exactly similar specimen, it will not be impermeable enough to prevent the appearance of blisters during the firing of the cover coat. This explanation would be applicable to iron L_2, 3–55 (Table 9).

An iron in which the gas evolution is sufficiently copious during the critical period will give numerous blisters even at the most favorable firing period, although the effect of the lower permeability of the ground coat at this period is appreciable. Iron L_2, 1–55, typifies this case (Table 9).

If gas evolution has practically ceased before the cover coat is fired, the added permeability of the ground coat at the longer firing periods has but little effect, though its overfired condition may be partially responsible for such blisters as do appear. Such an iron may be said to have a broad firing range. This case is typified by iron R_2, 2–56 (Table 9).

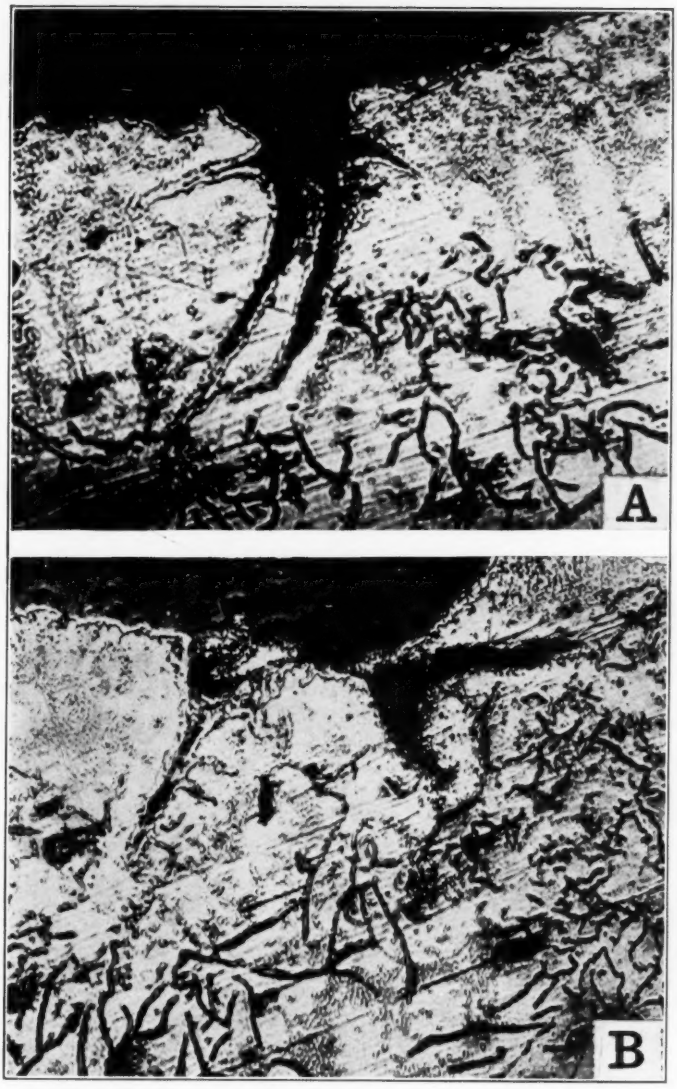

FIGURE 21.—*Etched cross section of surface of same iron shown (polished) in Figure 20*

Etched in 2 per cent HNO_3. × 500; *A* and *B* taken after enameling.

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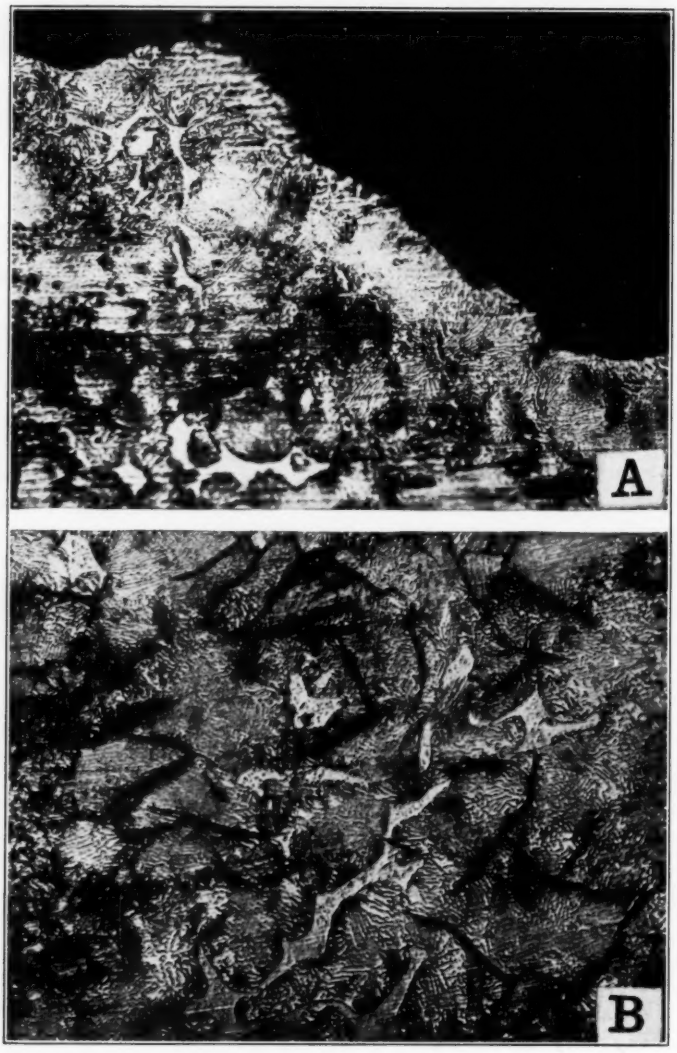

FIGURE 22.—*Cross sections at surface and interior of blistering iron before and after enameling. Iron L_1; heat 16*

Before enameling, etched in 5 per cent picric acid. × 500; *A*, surface layer at drag side; *B*, spot near center of casting.

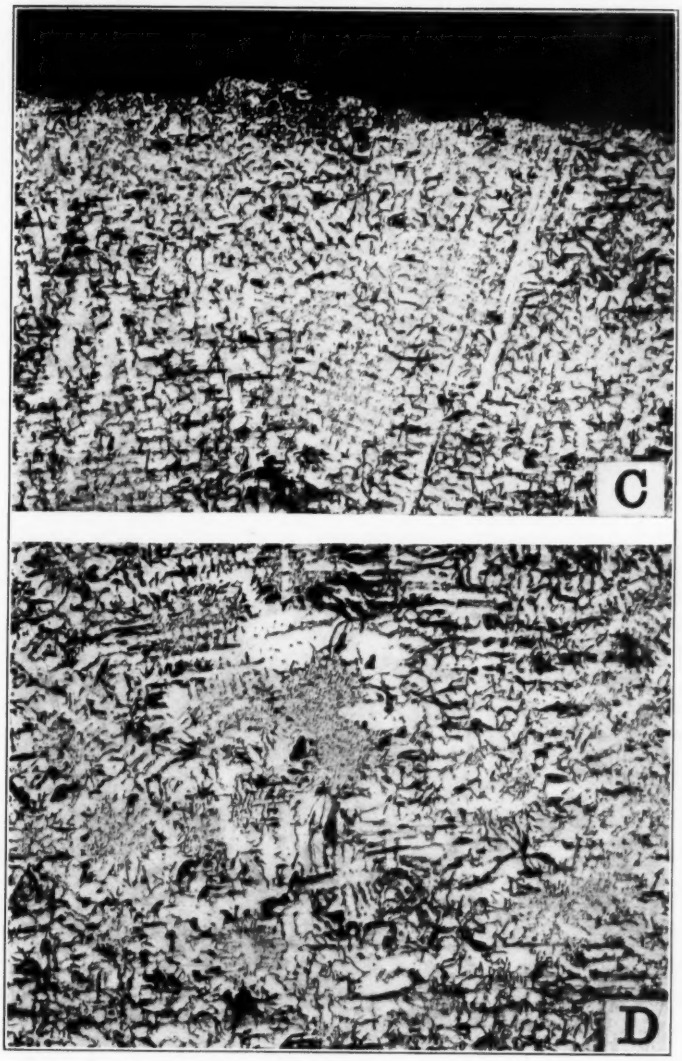

FIGURE 22.—*Cross sections at service and interior of blistering iron before and after enameling. Iron L_1; heat 16*—Continued

After enameling. Etched in 5 per cent picric acid. × 100; *C*, part of cross section adjacent to enamel; *D*, central part of cross section. A number of blisters were observed on this specimen. Ground coat fired 8 minutes at 870° C. (1,600° F.) and cover coat 7 minutes at 840° C. (1,545° F.).

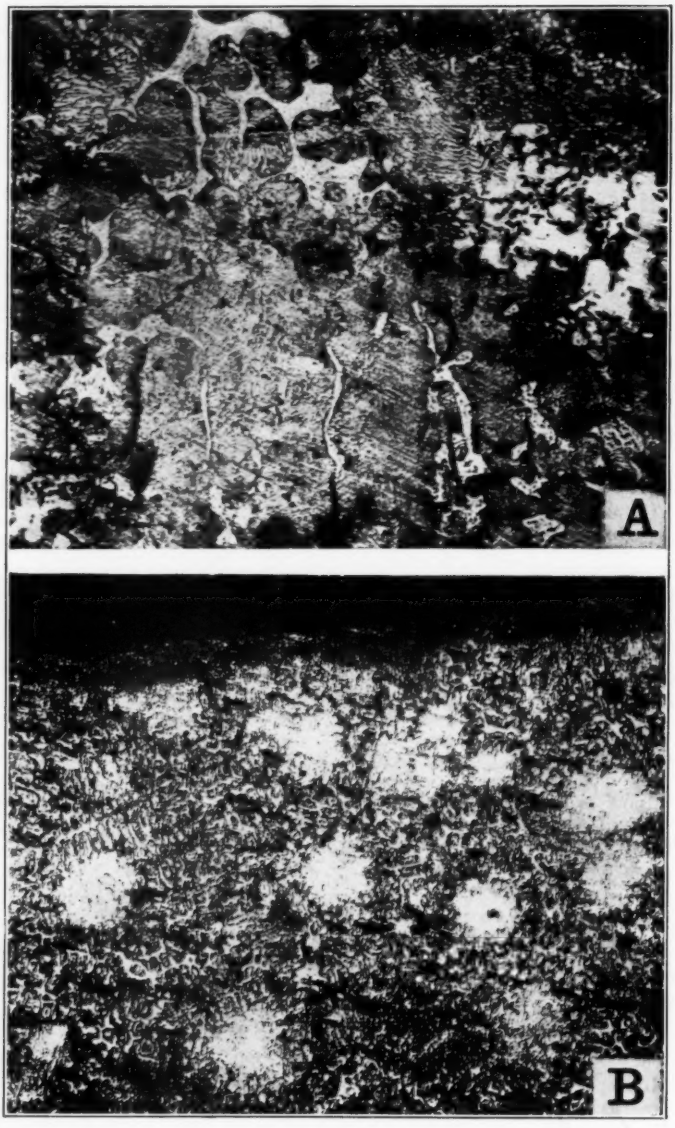

FIGURE 23.—*Cross sections of surface layer of nonblistering iron before and after enameling*

Carbon, 3.46 per cent; graphitic C, 2.85 per cent; combined C, 0.61 per cent; manganese, 0.52 per cent; phosphorus, 0.510 per cent; sulphur, 0.101 per cent; silicon, 2.22 per cent; etched in 5 per cent picric acid. *A*, Specimen before enameling. × 500; *B*, specimen enameled. × 100. No blisters were noticed on this specimen. Ground coat fired 5½ minutes at 900° C. (1,650° F.); cover coat fired 6 minutes at 840° C. (1,545° F.).

IX. STUDY OF CARBON IN THE MICROCHILLED SURFACE

All of the tests described above serve to indicate, if not to prove, that the blister-forming gas is not SO_2, hydrogen from the decomposition of steam, or nitrogen from the decomposition of iron nitride. In all probability, it is CO_2 and CO.

There is good evidence that the reactivity of different varieties of carbon and graphite varies very greatly with the ratio of surface to volume of the particles, and with the mode of formation of the particles. Falcke (26), for example, experimented with the rate at which amorphous carbon purified in various ways and purified natural graphite from different sources, reduced iron oxide in the presence of iron. The initial temperature at which reduction started and the rate at which it progressed varied markedly with the different varieties of carbon and graphite.

Moreover, the CO and CO_2 formed by the oxidation of any form of carbon will affect the rate of decomposition of cementite both by decarburization (27), which alters the amount of carbon, and hence its distribution between the graphitic and combined forms, and, according to Hayes (28), by a catalytic action.

It has been noted in commercial enameling that adhesion of enamel, for which a certain degree of oxidation of the surface of the iron is thought to be desirable, varies according to the size of the load with respect to the size of the furnace. This may indicate that there is not always enough oxygen available in the furnace atmosphere effectively to oxidize a large surface of graphite particles.

The weight of evidence strongly indicates that carbon in some one or more of the possible forms, ordinary graphite, submicroscopic graphite, "temper carbon," or combined carbon (cementite) plays a major rôle in the formation of blisters, and the problem appears to resolve itself into a study of carbon in the microchilled surface.

1. ORDINARY GRAPHITE

It is unlikely that massive graphite is responsible for blistering. It is true that finely divided graphite smeared on the surface of the iron as by writing on the iron with a pencil gives blisters, and that carbonaceous mold facings are probably to be avoided, though very light applications have been successfully used.

One might assume that in severe sand-blasting, which is known to minimize blistering, the graphite flakes may be dug out and removed, and leave a practically graphite-free surface. Microscopic examination, however, shows that graphite flakes may extend to the surface of the metal without causing blisters. (Fig. 19 (*c*).) On the other hand, graphite flakes may appear at the surface of a specimen which does blister. (Figs. 20 and 21.) Such flakes may cause local poor adherence of the enamel. However, poor adherence does not seem to be necessarily connected with blistering, which fact is illustrated in Figure 16.

Moreover, as Figure 9 shows, a machined surface of the blistering iron L_2 does not blister, and it is certain that machining does not drag out and remove all the graphite flakes. Massive graphite in itself can not be considered as invariably producing blisters.

2. SUBMICROSCOPIC GRAPHITE

The assumption was made that aside from the regular graphite particles, visible under high and low magnification, there are particles beyond the resolution of the microscope. On account of their small size, these particles should be very active and should readily respond to the heat; that is, they may agglomerate to somewhat larger groups or may burn away, depending upon the temperature used.

A certain confirmation of these data is given in the following statement by Ropsy (17); "In fact, in the hardened part of a chilled casting (cooled, therefore, very rapidly and solidified almost without transformation) there remains up to 0.15 per cent of carbon in the form of graphite. To effect this determination with precision, at least 5 g of metal must be dissolved, the determination of graphite being carried out on the residue. The microscope, even with the highest magnification, does not show this graphite, probably because it is disseminated throughout the mass in the form of particles which are too minute."

If these particles are, in fact, disseminated "throughout the mass," it is obvious that they could cause the evolution of gas even after the removal of the surface layer of a casting and may be responsible for a large evolution of gas in the first period of firing.

In fact it is probable that the comparatively rapid evolution of gas during the first 8 to 10 minutes of firing (fig. 18) is in all cases caused by the oxidation of these submicroscopic particles of graphite, which are presumed to be present in approximately equal concentration (*a*) in the surface layer of the weakly blistering iron, (*b*) beneath the surface of the weakly blistering iron, and (*c*) in the surface layer of the strongly blistering iron, but in greater concentration beneath the surface of the strongly blistering iron. In all cases the oxidation of this type of carbon is probably completed in the 8 to 10 minute period, and is not responsible for any subsequent evolution of gas.

3. COMBINED AND TEMPER CARBONS

As pointed out in the introduction, chilled iron, with practically all of the carbon in the combined form, has been said by some to blister and by others not to blister. It was thought that the explanation of this difference of opinion might lie in the individual conditions surrounding each observation, which in some cases tend to promote and in others to retard graphitization. These conditions are believed to include the degree of massiveness of the cementite formation, the presence or absence of elements which tend to stabilize cementite, superheating of the melt and other conditions. In order to throw some light on this question, the following experiments were carried out.

Samples of a white iron (plow shares)[4] were subjected to the standard enameling tests, and were found to blister badly over the whole range of firing temperatures. Specimens from which the surface had been deeply machined still blistered just as badly.

On annealing this white iron at 950° C. (1,740° F.) for five hours and cooling in the furnace, the tendency to blister was much reduced, the specimen tested at the shorter firing periods of the "range" method being practically perfect. The surface was decarburized by

[4] Donated by The Lynchburg Foundry Co., Lynchburg, Va.

the long heating. However, specimens from which the decarburized surface had been removed by machining, so that the enamel was applied on a surface that was not decarburized, were equally as good as those enameled on the decarburized surface. Such long annealing was not required since heating to 900° C. (1,650° F.) for 45 minutes followed by furnace cooling, was also effective in greatly diminishing blistering.

The annealing altered the structure decidedly by producing well agglomerated "temper carbon," that is, practically massive graphite. In the short heating of the enameling process, there was evident decomposition of cementite, but very little agglomeration. On the other hand, a specimen of malleable iron in which microscopic examination showed most of the "temper" carbon to be well agglomerated did not blister (rating 1) when the firing time of the ground coat was 7½ or 10 minutes, but did blister badly (rating 4 to 5) at 12½ and 15 minutes. Well agglomerated temper carbon thus appears nearly as nonreactive as massive graphite. The distinction between agglomerated temper carbon of malleable iron and massive graphite of gray iron is, therefore, probably one of appearance rather than of chemical activity.

The great activity of colloidally dispersed temper carbon, just as it forms and before it agglomerates is in sharp distinction to the lower activity of the agglomerated material.

In order to study a mild chilling effect on the weakly blistering castings, iron R_2 was cast in the usual three-sixteenths inch thick plates in a variety of sand molds as follows: (*a*) Skin dried; (*b*) moisture content, 6 to 7 per cent; (*c*) moisture content, 10 per cent. This heat was designated No. 65.

The specimens were enameled in the regular way save that the time of firing of the ground coat was 12½ minutes instead of 8 as heretofore, since the longer time of firing seemed to accentuate the tendency to blister. All specimens were graded No. 2 with respect to blistering. These results indicated that the variations in moisture content of molding sand used were not pronounced enough to cause chilling sufficient to affect the blistering tendency.

Some interesting results were obtained when definite chilling of the surface was resorted to. Strongly blistering iron L_2 and weakly blistering iron, R_2, were cast in blocks 3 by 6 by 2 inches in various ways, (*a*) in green sand, (*b*) against a chill plate covered by one-fourth inch of green sand, and (*c*) directly against a chill. Slices three-sixteenths inch thick were then cut from the blocks, the slice from the drag side being designated A and the next three-sixteenth-inch slice, B. The surfaces enameled were the drag face on A and on B the surface three-sixteenths inch from the drag side. The standard enamel with 12½-minute firing of the ground coat was used. The results are given in Table 25.

TABLE 25.—*Enamel ratings of iron specimens with chilled surfaces*

Specimen	Iron	Character of iron	Enamel ratings		
			Green sand	Sand over chill plate	Chill plate
A	L_2	Strongly blistering	4–5	4–5	4–5
	R_2	Weakly blistering	1–2	4	2–3
B	L_2	Strongly blistering	2	2	2
	R_2	Weakly blistering	2	2	4–5

Consider first the results in green sand. It will be noted that away from the surface, the body of the strongly blistering iron gives good enamel ratings. This is the equivalent of an ordinary strongly blistering test plate from which the microchilled surface has been machined. The weakly blistering iron behaves the same at the surface and in the interior, which observation is consistent with Figure 9.

When the surface was slightly chilled, by casting against one-fourth inch of green sand over a chill plate, the iron termed as "weakly" blistering took on a casting surface that was as poor as that of the iron termed "strongly" blistering. Removal of the surface produced the same improvement in both. Under such casting conditions the irons were identical in behavior as to blistering. Irons R_2 and L_2 did not appear very different in nature.

When the surface was more strongly chilled by casting directly against a chill plate, the strongly blistering iron acted just as it did with less severe chilling. However, the weakly blistering iron had less blistering tendency on the strongly chilled surface than it had on the corresponding weakly chilled surface (slice A, Table 25). In the interior, however (three-sixteenth inch from the drag surface) the severely chilled weakly blistering iron behaved on enameling practically the same as the drag side of the same when less severely chilled.

The decomposition of cementite from combined carbon to temper carbon or graphite which occurs in a chilled or microchilled layer during enameling will doubtless depend on (*a*) the original content of combined carbon, (*b*) the composition of the iron as to elements that promote or hinder graphitization, and (*c*) the time and temperature of enameling.

If all these conditions are such that there is no breakdown of combined carbon during enameling, it may be assumed that the iron does not blister. Under this assumption, either stable white iron, or stable gray iron would be "nonblistering." But, if the chilled layer contains combined carbon that does break down to colloidally dispersed temper carbon during a certain period of the enameling process, it will blister. If the enameling process is carried out at a high temperature and for a long time (for example, 15 or 17½ minute firing periods), the blistering tendency will be accentuated either because the combined carbon, although stabilized, may begin to break down under this treatment or because the graphite may begin to oxidize under such conditions. If the same iron is enameled with a shorter firing period, or at a lower temperature, or by using more fusible enamels, the iron may not blister.

Thus, the blistering for which combined carbon is responsible may be traced to the breakdown of combined carbon to temper carbon at a stage during enameling at which oxidation can occur and at which the enamel is in such physical condition as to retain the CO and CO_2 formed. If the breakdown at this stage is prevented, there will be no "nascent" temper carbon to cause blisters. It may be prevented by the nature of the chilled layer itself, or by removing the offending surface layer, or avoiding conditions that will produce this layer, or decarburizing the surface, or by accomplishing the breakdown before the enameling operation.

To recapitulate, stable cementite is not necessarily readily oxidized to give the CO_2 or CO gases that appear to be responsible for blistering. Neither does massive graphite, whether formed as such during

solidification and cooling of gray iron, or as a product of decomposition of cementite on annealing, appear responsible for blistering. It does appear, however, that an intermediate structure, resulting from the partial breakdown of cementite on annealing and partial agglomeration to graphite is the most active in producing blisters.

The enameling process itself is a short anneal. The decomposition of cementite will be accelerated by the presence of graphite in the original casting. Agglomeration of small, widely distributed particles of primary graphite into larger flakes is shown by Figure 19 (*a*), (*b*), (*c*), in which the progressively increased agglomeration of graphite particles with increased firing periods is very plain. Even the body of a gray-iron casting is changed in structure and hardness by the heat-treatment incidental to enameling.

4. CHANGE OF HARDNESS AND STRUCTURE ON ENAMELING

Table 26 shows the decrease in hardness that takes place on enameling. Metallographic examination of a number of specimens showed that a considerable change in the structure of the iron occurred during the enameling process and this change often was not confined to the surface layer, but took place throughout the section of the specimens. A specimen which before enameling contained a lamellar pearlite matrix throughout its section (figs. 22 (*A*) and (*B*)), showed, after enameling, the large ferritic areas and dendritic structure similar to those represented in Figures 22 (*C*) and (*D*). The remainder of the pearlite was usually spheroidized or changed to sorbite.

It was noted that some specimens of weakly blistering iron appeared to undergo no change detectable under the microscope during enameling. Figure 23(*B*) at ×100 shows a weakly blistering specimen, the surface of which when examined at ×500 after enameling appeared to be unchanged from the pearlitic structure of the unenameled specimen shown in Figure 23(*A*). It was thought for a time that a lower blistering tendency might be associated with a smaller change in structure, but it was found later that this was not always true and that a marked change in structure often occurred in weakly blistering as well as in strongly blistering specimens.

Much attention was paid to the "habit" of the graphite (17); that is, whether it was in fine flakes, only slightly agglomerated, or almost entirely agglomerated in the "whirl" form, but the observations seemed to justify the conclusion that the habit of the graphite is not definitely associated with the blistering tendency.

5. BURNING OUT

The familiar "burning out" or normalizing in air so often resorted to by the enameler to prevent blistering may be considered as accomplishing various things: (*a*) It removes some of the surface layer of metal by oxidation, (*b*) it tends to decarburize, and hence, soften the layer of metal immediately beneath the oxide coat; (*c*) it softens the metal as a whole. Hence, when a "burned-out" casting is sandblasted, the loose oxide comes off readily, and the surface, now softer than before annealing, is more readily removed by sandblasting.

TABLE 26.—*Change in hardness of iron during enameling*

Iron	Melts	Heat No.	Carbon			Mn	P	S	Si
			Total	Graphite	Combined				
			Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
L_1	Cupola	6	3.65	2.97	0.68	0.56	0.46	0.05	2.16
L_1	do	14	3.47	3.07	.40	.57	.46	.076	2.24
L_1	Cupola, melted 3 times	16	3.47	2.95	.52	.33	.47	.095	1.92
L_1	Cupola with 0.1 per cent S in the ladle.	22	3.59	2.99	.60	.56	.45	.121	2.22
L_1	Electric furnace	17	3.76	3.10	.66	.63	.47	.038	2.19
L_1	Electric with 0.1 per cent S in the ladle.	20	3.81	3.09	.72	.65	.45	.10	2.13
L_1	Electric with 0.13 per cent S charged with iron	28	3.67	3.09	.58	.61	.43	.092	2.21
R_1	Cupola	7	3.40	3.18	.22	.69	.81	.048	2.82
R_1	Electric with 0.16 per cent S added to molten iron in the furnace	26	3.58	3.09	.49	.77	.79	.09	2.93
L_2	Electric	44	3.60	3.15	.45	.71	.49	.043	2.44

Iron	Melts	Heat No.	Hardness before enameling		Hardness after enameling		Decrease in hardness	
			Shore scleroscope	Rockwell B scale	Shore scleroscope	Rockwell B scale	Shore scleroscope	Rockwell B scale
							Per cent	*Per cent*
L_1	Cupola	6	47.4	96.2	33.9	79.8	28.5	17.0
L_1	do	14	48.4	93.2	35.7	76.8	26.2	17.6
L_1	Cupola, melted 3 times	16	50.4	96.8	35.1	81.3	30.4	16.0
L_1	Cupola with 0.1 per cent S in the ladle	22	47.3	95.6	36.4	81.1	23.0	15.1
L_1	Electric furnace	17	43.4	89.4	33.0	81.3	24.0	9.1
L_1	Electric with 0.1 per cent S in the ladle	20	46.8	93.8	32.9	80.5	29.7	14.1
L_1	Electric with 0.13 per cent S charged with iron	28	46	94.6	33.1	82.5	28.0	11.1
R_1	Cupola	7	46	94.6	40.9	89.7	11.1	5.2
R_1	Electric with 0.16 per cent S added to molten iron in the furnace	26	42.6	92.2	35.8	77.3	15.9	16.2
L_2	Electric	44	46.5	93.3	38.5	75.7	17.2	19.0

6. EFFECT OF ELEMENTS IN CAST IRON ON CHILLING TENDENCY

The formation of the microchill appears to be a matter of delicate balance, as is evidenced by Table 9, where some heats of the "strongly blistering" northern iron are shown to be better than some heats of the "weakly blistering" iron.

The question then arises, can the composition of the "blistering" irons be so adjusted that the microchill will not form, or will not be too deep and too hard for complete removal by ordinary sand-blasting. In order to bring this about, it would be quite natural to add some element that would tend to foster graphitization and prevent the retention of combined carbon. The addition of silicon, aluminum, or nickel (well-known graphitizing agents) as previously discussed, indicated that some improvement may be accomplished by such means, particularly in the case of silicon if added in the proper manner and proportion. The "microchill" appears to be more difficult to prevent than the ordinary chill, which can be readily controlled by properly adjusting the composition and the rate of cooling. However, it seems reasonable that all changes that tend to prevent the formation of the ordinary chill would also be steps in

the right direction in the prevention of the "microchill." We may, therefore, turn to a brief consideration of the effect of the various alloying elements on the chilling of cast iron; that is, the formation of combined carbon.

Gray cast iron, such as is used for enameling, contains carbon, silicon, sulphur, manganese, and phosphorus besides small amounts of other elements. The properties of the iron are very greatly affected by the condition of the carbon, and this is controlled as much by the rate of cooling as by the composition. When the metal freezes, the carbon is in combination with iron, as the compound Fe_3C (cementite). Manganese, chromium, or other carbide forming elements form similar carbides, and cementite will normally be contaminated with more or less of those carbides. If the metal is chilled very rapidly, the cementite is retained without decomposition, and white or chilled iron which is practically free from graphite will result. Cementite is brittle and hard and since white cast iron contains so much cementite it is extremely brittle and hard.

If the metal is allowed to cool more slowly, during and after solidification, some of the cementite will decompose and form iron (ferrite) and free carbon (graphite or temper carbon). The resulting product, "gray iron," is much softer than white iron.

The total amount of carbon in ordinary cast irons does not vary very much, but the relative amounts of free carbon and of combined carbon (cementite) do vary greatly, not only with the rate of cooling, but also with the other elements present.

(a) SILICON

At a given rate of cooling, a higher silicon content is favorable toward a higher graphite and a lower combined carbon content. The silicon content is the chief factor controlling the ratio of graphite and combined carbon and the chief agent in securing soft gray iron instead of hard white iron.

(b) PHOSPHORUS

Phosphorus is alleged (21) to foster graphitization and thus tend to make soft iron. But iron phosphide itself is hard and brittle so that a high phosphorus iron tends to be hard, notwithstanding the increased precipitation of graphite. The iron phosphide has a low melting point, and the fusibility of the iron is much increased by increase in phosphorus. Since the melting point is lower the pouring temperature can be lower, and hence the rate of cooling will be altered. The action of phosphorus is, therefore, complex.

(c) SULPHUR AND MANGANESE

Sulphur tends to oppose the precipitation of graphite, especially when present as iron sulphide. If sufficient manganese is present, the sulphur will be combined as manganese sulphide, which is more inert in its effect on precipitation of graphite. The ratio of manganese to sulphur therefore, governs the effect of the sulphur up to the point (often taken as 7:1) where manganese is in decided excess of the amount necessary to force practically all the sulphur into manganese sulphide. Up to this point, then, manganese is in a way a softener because of its effect on sulphur.

Shaw (19) denies that manganese aids the retention of carbon as cementite and ascribes the increased Brinell hardness to the effect of manganese in altering the microstructure, the matrix tending to be sorbitic and the graphite in "whirl" form. Parker (22), however, insists that manganese does increase the stability of the carbide. The effect of increased sulphur in slowing down the rate of graphitization of white cast iron, and the counteracting effect due to manganese additions is brought out by Hayes and Flanders (23) and others (24).

Cupola remelting would be expected (Table 1) to lower the silicon and manganese somewhat and to raise the sulphur, with consequent decrease in the ratio of manganese to sulphur. This change is accompanied by an increase of combined carbon which causes a hardening of the iron. Cupola remelting would thus be expected to act in a detrimental manner rather than a beneficial one on blistering. No satisfactory evidence has been obtained in support of the idea that remelting was beneficial.

Manganese in excess of the amount required to combine with sulphur, however, is usually considered a hardener, which forms a stable, manganese-bearing cementite and increases the depth of chill. Guedras (25) says that in black-heart malleable castings the formation of a finely dispersed type of temper carbon rather than of large graphite particles is favored by the stabilizing action of manganese upon cementite.

The graphite precipitated from cementite as the casting cools presumably appears first as very finely divided, even submicroscopic, "temper carbon," which is chemically and structurally the same as massive graphite, but very much more finely divided, hence, much more reactive.

X. SUMMARY

The data obtained in this investigation support the explanation of blistering which is summarized in the following paragraphs, and which is the only one known to the authors that fits the facts so far observed.

1. There is ample evidence that physical defects, especially "sponginess," will give rise to blisters. Moreover, an enamel may be composed, prepared, or applied in such a manner as to cause blisters irrespective of the character of the iron used. There are, however, differences in the tendencies of sound castings, made from different lots of iron or made from the same iron under different conditions, to give blisters when enameled under identical conditions. The gases forming the blisters are CO and CO_2.

2. A gray iron casting of the composition normally used for enameling acquires in freezing and cooling in the mold a very thin surface skin, which may be considered as a "microchill." This layer extends only a few thousandths of an inch below the surface and varies in thickness, hardness, and resistance to abrasion by the sand blast. Removal of this surface layer eliminates blistering except such as is caused by sponginess or other physical defects which extend more deeply into the interior. The analyses of the surface layers indicate that the hardness and resistance to abrasion may be due either to the higher combined carbon or to some other hard component.

3. The cementite (combined carbon) of this skin tends to break down, during the enameling process, to very finely divided "temper carbon." This form of finely divided carbon is more readily oxidized, as would be expected from its fineness, than massive graphite or combined carbon.

4. This breakdown to a readily oxidizable form of carbon, analagous to the early stages of the malleableizing of white iron, leads to the formation and evolution of CO and CO_2, upon heating, which causes greater or less damage, according to the stage of the enameling process at which it occurs. If the enamel coat is sufficiently fused to form the gas into bubbles, but not fluid enough to heal after any bubbles of gas have escaped, blisters will occur. If the craters partially heal, there will be dimples. If the enamel is a low melting one, applied at a low temperature, the annealing action coincident with enameling may not be sufficient to produce a breakdown of the cementite accompanied by the formation of the finely dispersed temper carbon, or, if it is produced and CO and CO_2 are formed, the enamel may be fluid enough to allow the gas to escape without damage.

5. There are probably two kinds of nonblistering iron, one in which a small amount of combined carbon is present in the surface layer, and the other in which cementite is so stable that it takes a relatively long time to break it down into ferrite and temper carbon.

6. Decarburization of the skin, as well as its removal by mechanical or chemical means, will eliminate the source of temper carbon. Hence, blister-free ware can be obtained with a sound casting if the enameling process itself is properly carried out, unless the whole casting is of such a nature that the body as well as the skin will give temper carbon on enameling. Some irons have a greater tendency to give the microchilled layer than others. The gas evolution which apparently takes place during the first part of the firing treatment, even from those specimens having the least blistering tendency of any studied, has been assumed to be due mainly to submicroscopic graphite, which burns out too quickly to cause blisters.

7. Aside from such variations as may be attributed to differences in enameling procedure at the different plants, the presence of a hard surface layer or "microchill" probably accounts for most of the inconsistencies observed in the early part of the investigation, as well as those between the results of various laboratories. Unless sand-blasting was uniformly controlled and the surface layer uniformly attacked, it is obvious that erratic results would be obtained on enameling.

8. Attempts to nullify the hardening effect of sulphur by addition of manganese do not appear to offer much hope, since excess manganese is in itself harmful. Addition of some graphitizing agents, such as silicon, or any precaution in casting that will tend to minimize the tendency to chill, may be beneficial, but it is much more difficult to prevent the formation of the microchill than the formation of the well understood ordinary or macrochill.

9. In cases when an occasional heat or lot of sound castings show a tendency to blister, "burning out," or deep sand-blasting, appears to be the most practical remedy.

XI. ACKNOWLEDGMENTS

While this investigation was first undertaken by the bureau in 1922, in cooperation with the research committee of the enamel division, American Ceramic Society, under its chairman at that time, R. R. Danielson, the present enlarged cooperative plan of work which this report covers was instituted in 1924 jointly by the ceramics and metallurgy divisions of the bureau and the enamel division research committee, under the chairmanship of H. F. Staley, with some 36 enameling and other interested companies cooperating through the committee. More recently R. R. Danielson has again served as chairman of the enamel division research committee, to the many members of which grateful acknowledgment is made for their assistance in planning and furthering the work.

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WASHINGTON, September 13, 1929.

ON A MODIFIED METHOD FOR DECOMPOSING ALUMINOUS SILICATES FOR CHEMICAL ANALYSIS

By A. N. Finn and J. F. Klekotka

ABSTRACT

Evidence has been obtained that certain silicates of alumina and allied compounds, especially ceramic materials, can be decomposed for chemical analysis with relatively small amounts of Na_2CO_3. Satisfactory decomposition has been obtained by heating a 0.5 g sample with 0.6 g of Na_2CO_3 at 875° C. for two hours.

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I. INTRODUCTION

The decomposition of aluminous silicates for chemical analysis is usually effected by fusing 1 part of the powdered sample with from 4 to 18 parts of Na_2CO_3. W. F. Hillebrand [1] points out that "the larger amounts (of flux) introduce more impurity than the smaller and necessitate longer washing of precipitates," and that one of the disadvantages in the use of alkali carbonates is "the annoying interference of several grams of foreign fixed salts, which are most troublesome in that part of the analysis devoted to the separation of silica, alumina, iron, lime, and magnesia." In preparing certain silicates of a high alumina content for analysis, Lundell and Hoffman [2] found it necessary to use approximately 18 parts of flux to 1 of sample, and they discuss at length the errors introduced by incomplete decomposition and the subsequent incomplete removal of fixed salts.

In addition to other recognized but infrequently used methods for decomposing silicates for analysis, the literature, especially that referring to patents, contains many suggestions for breaking up silicates to obtain, commercially, one or more of their individual constituents. Many of the suggested methods can not be used for analytical purposes because they involve the use of undesirable fluxes, or do not produce complete decomposition. However, some patents are based on decomposition effected by sintering siliceous materials with small amounts of Na_2CO_3. Furthermore, the decomposition of argillaceous limestones by heating them with small amounts of Na_2CO_3 is recommended by several authors.[3] Hitherto, the use of relatively small amounts of flux has had but limited application in

[1] Bulletin 700, U. S. Geological Survey, The Analysis of Silicate and Carbonate Rocks, pp. 95 and 90; 1919.

[2] Research Paper No. 5, B. S. Jour. Research, Analysis of Bauxite and of Refractories of High Alumina Content; July, 1928.

[3] Among these are P. W. Shimer, R. K. Meade, and W. F. Hillebrand.

analytical chemistry except in the cement industry, and P. H. Bates, of this bureau, suggested the possibility of extending this method to the analysis of ceramic materials. Since the literature does not contain, as far as the authors of this paper have been able to learn, specific references to the use of what might be called a "sintering method" for decomposing silicates for analysis (except, of course, the time-honored J. Lawrence Smith method for determining alkalies), a series of tests were made to determine the feasibility of using very small amounts of Na_2CO_3 for decomposing ceramic silicates.

II. EXPERIMENTAL PART

Initially, several attempts were made to decompose silicates for chemical analysis by heating 0.5 g samples with equal amounts of Na_2CO_3 in platinum crucibles over gas flames. Promising results were obtained, but it soon became apparent that heating at definite temperatures would probably give better results. Consequently, an electric muffle furnace was used, and temperatures were determined with a thermocouple connected to a portable potentiometer.[4] Conditions were then modified by varying the amount of Na_2CO_3 used, the time of heating, and the temperature. It then became evident that the majority of samples tested decomposed readily after heating with Na_2CO_3 at about 875° C. for two hours.

The results obtained under several conditions and the silica and alumina content of the materials used are given in Table 1. For comparison, the table also contains the weights of the nonvolatile residues obtained after the samples had been decomposed by fusion with the larger amounts of Na_2CO_3 ordinarily used. The materials referred to by numbers may be described as follows: Nos. 69, 70, 76, 77, and 78 represent standard samples prepared especially for the ceramic industry by the Bureau of Standards; of these No. 69 is bauxite, No. 70 is feldspar, Nos. 76, 77, and 78 are burnt refractories; No. 3 is a "flint clay"; No. 5 is a "bond clay"; No. 12 is a "crushed quartz"; No. 17 is a "siliceous brick"; M–1, M–2, and M–3 indicate routine samples which were analyzed after sintering, and their compositions and treatments are included in the footnotes to the table.[5]

The sample and Na_2CO_3 were placed in a platinum crucible and thoroughly mixed by stirring with a glass rod. Intimate grinding in a mortar did not affect the final result materially, so in most of the work the simpler method of mixing was used. The addition of a few drops of alcohol and 1 or 2 ml of water to the two unmixed materials should be beneficial by bringing about more intimate contact between the clay and Na_2CO_3, but, on drying, segregation often occurs and produces undesirable results. However, a few good sinters were obtained after such a treatment.

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[4] Attention is directed to the fact that temperatures in all parts of the muffle may not be the same as that indicated by a thermocouple placed in any one position.

[5] Although the data contained in Table 1 are based on 2-hour treatments, some evidence was obtained that certain silicates can be decomposed in much less time.

TABLE 1.—*Degree of decomposition effected by various sintering treatments for two hours as indicated by amount (g) of nonvolatile residue obtained from 0.5 g samples after treating dehydrated SiO_2 with HF and H_2SO_4*

Sample No.	Partial composition		Temperature and amount of Na_2CO_3 used											Nonvolatile residue after ordinary fusion [1]
	SiO_2	Al_2O_3	825° C. and 0.5 g Na_2CO_3	825° C. and 0.7 g Na_2CO_3	850° C. and 0.5 g Na_2CO_3	850° C. and 0.6 g Na_2CO_3	875° C. and 0.7 g Na_2CO_3	875° C. and 0.6 g Na_2CO_3	875° C. and 0.5 g Na_2CO_3	875° C. and 0.4 g Na_2CO_3	900° C. and 0.3 g Na_2CO_3	950° C. and 0.3 g Na_2CO_3	950° C. and 0.2 g Na_2CO_3	
	Per cent	*Per cent*												
76	54.68	37.67	0.0139	0.0041	0.0068 .0133	0.0052	[2] 0.0026	[3] 0.0269 .0027 .0025	0.0035	[2] 0.0109	0.0178	[2] 0.0118	[2] 0.0319	0.0060 (3)
77	32.38	59.39	----------	.0061	.0049 .0068	.0030	.0018	.0014 .0023 .0009	.0029	.0091	.0442	.0356	.1099	.0044 (3)
78	20.69	69.97	.0130	.0091	.0115 [2] .0892	.0042	.0009	[3] .1279 .0024 .0004	.0089	.0211	.0661	.0616	.1619	.0060 (2)
60	6.32	55.06	.0002	[4] .0037	.0038 .0032	.0029	----------	.0008	.0010	.0003	.0044	.0022	.0464	----------
70	66.66	18.03	.0009	[2] .0006	[5] .0013 [5] .0022	[2] .0075	----------	[5] .0006	----------	----------	----------	----------	----------	.0025 (3)
3	47.12	46.76	----------	----------	.0149 .0228	.0091	[2] .0035	.0038	.0105	.0164	.0032	[2] .0308	.0334	.0076 (4)
5	63.48	31.91	----------	----------	.0157 .0164	.0393	.0049	.0035	.0058	[2] .0174	[2] (x)	[2] .0114	[2] (x)	.0062 (2)
12	69.12	27.08	.0080	.0099	.0018 .0121	.0133	.0026	.0038 .0010	.0010	----------	----------	----------	----------	.0084 (2)
17	80.12	17.18	[2] .0139	.0051	[2] .0135 [5] .0098	.0063	.0027	[5] .0027 [2] .0038	[5] .0071	[5] .0259	[5] (x)	[5] (x)	[5] (x)	.0019 (1)
M-1	----------	----------	----------	[4 5 6] .0015	[7] .0018	[7] .0022	[8 9] .0009	[8] .0002	----------	----------	----------	----------	----------	[7] .0034 (1)
M-2	----------	----------	----------	[6 10] .0019	----------	[11] .0011	----------	----------	----------	----------	----------	----------	----------	[11] .0088 (1)
M-3	----------	----------	----------	[6 12] .0004	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------

[1] The figures in this column represent the average nonvolatile residues obtained from silica after the samples had been fused with Na_2CO_3 in the ordinary or generally recognized method. The figure in parentheses is the number of determinations on which the average is based.
[2] Partially vitrified.
[3] Temperature too low due to position of sample in muffle. (See footnote 4.)
[4] 0.3 g Na_2CO_3 used.
[5] Fused.
[6] Feldspar No. 70.
[7] Glacial clay (65 per cent SiO_2, 14 per cent Al_2O_3, 5.5 per cent Fe_2O_3).
[8] Kaolin (46 per cent SiO_2, 37 per cent Al_2O_3).
[9] 0.2 g Na_2CO_3 used.
[10] 0.5 g Na_2CO_3 used.
[11] Shale (57 per cent SiO_2, 19 per cent Al_2O_3, 8 per cent Fe_2O_3).
[12] 1.0 g Na_2CO_3 used.
x Sinter unsatisfactory; discarded.

III. NATURE OF THE SINTER AND ITS SUBSEQUENT DECOMPOSITION

The word "sinter," as used in this report, refers to the product obtained after heating a mixture of the siliceous material with a small amount of Na_2CO_3. If the sample has been properly decomposed by the sintering treatment, the most desirable condition of the sintered material is that it be very friable or easily and completely broken up by very slight pressure with the flat end of a glass rod. Sinters have been obtained which after only very limited stirring were almost as finely divided as the original material. Less friable sinters are frequently obtained and they may also be quite vitreous or even distinctly glassy. If the sinter is very friable (as in the case of Nos. 69 and 78), no difficulty is encountered in decomposing it with water and HCl; if it is vitreous (Nos. 17 and 76), careful grinding with a glass rod before and during acid treatment is necessary; and if it is glassy (No. 70), digestion with water and HCl with frequent grinding readily effects decomposition. The addition of 1 or 2 ml of water to the sinters, previous to the addition of acid, promotes disintegration; this can be further facilitated by mild grinding with a blunt glass rod to break up the larger particles.

There are, of course, exceptions to the above conditions because at times vitrified or glassy masses are obtained which are so resistant to mechanical and acid treatment that they can not be satisfactorily handled. When these conditions are encountered, a change in either or both the amount of flux and temperature of sintering may yield a workable sinter, but a change in sintering conditions does not always appreciably affect the degree of decomposition. This may be seen in the data of Table 1, which indicate that the decomposition of sample No. 69 (bauxite) was quite satisfactory under a wide range of conditions. In this connection it should be stated that satisfactory results were obtained when bauxite was mixed with 0.5 g Na_2CO_3 and heated directly over the full flame of a Fisher burner. Furthermore, the sample of "kaolin" (footnotes 8, 9, and 8, in line M–1 of table) reacted well at 875° C. with 0.2 and 0.6 g Na_2CO_3.

The amount of insoluble residue, aside from the separated silica, remaining after the HCl treatment indicates qualitatively the degree of decomposition.[6] [7] The "degree of decomposition" (sometimes contracted to "decomposition") is measured by the amount of nonvolatile material remaining in the crucible after the dehydrated SiO_2 has been volatilized with HF in the presence of H_2SO_4. It was felt that this criterion could be used safely because in the ordinary analysis of silicates a few milligrams of residue are almost invariably found after volatilizing the dehydrated SiO_2. If, therefore, the residue after sintering was not excessive, decomposition was regarded as satisfactory. Hence, since the procedure following the weighing of the nonvolatile matter was not a part of this investigation, analysis was, in general, discontinued at this point.

[6] Bauxite and refractories of a high alumina content give a sludge on the addition of a little acid, which might be interpreted as very incomplete decomposition, but this sludge readily dissolves in excess acid.
[7] G. E. F. Lundell suggests that a slight residue may be caused by a recombination of some of the constituents.

IV. RECOMMENDED PROCEDURE

In view of the foregoing statements, the following procedure is recommended for applying the sintering method to the decomposition of certain silicates for chemical analysis. Only the essential details of the sintering method will be given, and for other details the reader should consult the paper on the Analysis of Bauxite and of Refractories of High Alumina Content, by Lundell and Hoffman.[8]

Thoroughly mix 0.5 g of the powdered material and 0.6 g of powdered anhydrous Na_2CO_3 in a platinum crucible by stirring them with a glass rod for at least five minutes. Heat the covered crucible and its contents at 875° C. for two hours. Cool, add 1 or 2 ml of water, digest for about 10 minutes, and then stir, or grind if necessary, to break up all particles as completely as possible. Wash the contents of the crucible into a beaker or casserole, using not more than 50 ml of water. Heat to boiling, and with constant stirring, rapidly add about 20 ml of concentrated HCl (specific gravity 1.19). Crush any gritty particles that remain as much as possible with a glass rod and evaporate the solution to dryness.[9] Finally heat at 105° to 110° C. for one hour to complete the dehydration of the SiO_2. Cool, add 20 ml of HCl (specific gravity 1.19), digest until effervescence of HCl ceases, add 100 ml of water, boil or digest with occasional stirring until all the aluminum compounds are in solution, filter through a 7 cm No. 40 Whatman or similar paper, and wash the precipitated SiO_2 first with hot dilute HCl (5 parts of concentrated HCl and 95 parts of water) and finally with hot water. Ignite the SiO_2 to constant weight and treat it with HF and H_2SO_4 in the usual way. Heat the residue and correct the initial weight of the SiO_2 accordingly. For more precise work, a second evaporation for residual SiO_2 should be made.

V. CONCLUSION

Although the work described in this paper is based on tests of a relatively few kinds of aluminous silicates it is thought that the method can be applied to other silicates by proper adjustments of the relative amounts of sample and Na_2CO_3 used, and the time and temperature of sintering. It should be especially useful to chemists who frequently analyze materials of the same general nature, because after having determined the particular conditions best suited to sintering their samples, the time required for thoroughly decomposing the sample will be shortened with no sacrifice of accuracy. In fact, the accuracy may be increased because the solvent action of excessive amounts of NaCl on silicic acid in HCl solution is largely eliminated, and the amount of foreign salts to be washed out of precipitates is greatly reduced.

WASHINGTON, January 30, 1930.

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[8] This paper was published in the B. S. Jour. Research as Research Paper No. 5, July, 1928. Copies can be obtained from the Superintendent of Documents, U. S. Government Printing Office, Washington, D. C., price 5 cents.

[9] Frequent stirring facilitates evaporation.

TEST OF COMPOSITE BEAMS AND SLABS OF HOLLOW TILE AND CONCRETE

By D. E. Parsons and A. H. Stang

ABSTRACT

Sixty reinforced beams (or slabs), 12 being of concrete and 48 being composite beams representing portions of concrete and hollow tile slabs, were fabricated and tested in the laboratory to determine the value of the tiles in assisting the concrete to resist shear and bending. Among the variable features entering into the construction of the beams were included tiles of different qualities and weights and differences in their position in the beams. The shearing strength of the bond between concrete and hollow tiles was determined also by the testing of 120 specimens representing small portions of hollow tile and concrete slabs.

The results of the beam tests indicated that one row of tiles was equivalent in resisting shear to a concrete rib of the same depth and having a width of from 1.6 to 2.4 inches. At loads considerably less than the maxima the tiles were more effective in increasing the resistance of the beams to bending deformations than at the higher loads. The relatively lower values for the higher loads are believed to be due at least in part to partial failure of the bond between the concrete and tiles.

The strength in shear of the bond between concrete and hollow tile was found to be affected by the factors having an influence on the compressive strength of the concrete. This strength was greatest when concrete containing the least amount of water necessary for its proper placement was used in combination with dry or slightly dampened tiles. The results indicated that the methods followed in the construction and aging of the beams were not favorable to the development of as strong a bond as would have been obtained with different methods.

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I. INTRODUCTION

Investigations [1] have shown that hollow-tile fillers add materially to the strength of concrete floors of ribbed construction. Although this is not the chief function of the tiles, it is of obvious economy to take account of their structural values in designing such structures. In attempting to establish a safe allowance for the tiles, the designer is confronted with problems which can not be solved by analysis alone. For information on the strength of the bond between concrete and hollow tile and on the relative values of tiles of different designs and different materials, he must depend upon the results of service and laboratory tests.

In 1924 the Bureau of Standards, cooperating with the Hollow Building Tile Association, completed a series of tests [2] on beams (or slabs) made to represent portions of combination hollow tile and concrete slabs of the 1-way type. Since one of the objects of that investigation was to obtain data on the strength of field-made structures, the beam specimens were built by a contractor who followed the methods commonly used in the construction of buildings for speculation. In that series materials for the concrete in the test beams were not carefully proportioned, and the contractor was permitted to employ without interference the usual rush methods of construction. This procedure was followed in order to lessen the probability of obtaining unduly favorable values which might have resulted from tests of carefully made laboratory specimens.

In a second series of similar tests, completed in 1926, the beam specimens were made under laboratory control in order to minimize variations in the results due to unknown causes. This paper is a report on the second investigation. These later tests deal with the same type of construction and supplement the former series, but some of the specimens were not representative of commercial construction

[1] Slater, Hagener and Anthes, Tests of a Hollow Tile and Concrete Floor Slab Reinforced in Two Directions, B. S. Tech. Paper No. 220. Larson and Petrenko, Loading Test of a Hollow Tile and Reinforced Concrete Floor of Arlington Building, Washington, D. C., B. S. Tech. Paper No. 236. Parsons and Stang, Tests of Hollow Tile and Concrete Slabs Reinforced in One Direction, B. S. Tech. Paper No. 291.

[2] Reported in B. S. Tech. Paper No. 291

either in design or in workmanship. It is thought, however, that, owing to the care used in the construction of the specimens for the later tests, the results give more reliable comparisons between the effectiveness of different types and qualities of tiles than would normally be obtained with specimens constructed under methods used in the first series.

Test data on the relative values in resisting stresses of the outer shells and the interior webs of tiles had not been obtained. Such information was needed as a basis for specifications for floor tiles and as an aid in the selection, from the many varieties manufactured, of a few designs best adapted for use in floor construction. Information was lacking also on the effect of the arrangement of the tiles on the strength of floor slabs and on the factors which govern the strength of the bond between concrete and hollow tiles. Test data relative to these subjects were obtained in the second investigation. Values were obtained for the strength of the bond between concrete and hollow tiles and information on the effects of the following factors on the value of hollow tiles in adding to the strength of tile and joist construction: (1) Quality of the tiles, (2) their weight, (3) number of cells, and (4) the position of the joints in adjacent rows.

The authors are indebted to W. A. Slater, then of the bureau staff, and to F. J. Huse, formerly chief engineer of the Hollow Building Tile Association, for their assistance in planning the investigation. Acknowledgements are due also to the Hollow Building Tile Association (now the Structural Clay Tile Association) for furnishing the materials and labor used in constructing the beam specimens. The bond tests were made by J. C. Oleinik, of the Bureau of Standards.

II. THE TEST BEAMS

1. TYPES

In general, each of the test beams consisted of either 1 or 2 reinforced concrete ribs (beams) similar to those in floors of concrete and hollow tile. Because of differences in the general types of construction represented and in the objects of the tests, the 60 beams included in the investigation are not all comparable with each other. For convenience in conducting the tests and in comparing the results, they are divided into three series—namely, series A having 27 beams, series B with 18, and series D with 15.

The specimens of all series, however, were similar in some features. The materials used in their construction were alike except the tiles; the concrete ribs in all combination beams were 4 inches in width; all were 8 inches in depth and contained two ⅞-inch diameter round steel bars in each rib for tensile reinforcement. In each series there were comparison beams of concrete which were identical in size and design to the concrete portion of either one or two of the ribs of the combination beams of the same series. The dimensions and details of the beams are shown in Figures 1 and 2. Photographs taken after test of one beam of each type are shown in Figures 5, 6, and 7. Table 1 gives the type of hollow tiles used in each beam. Photographs of samples of the tiles are shown in Figure 3. In designating the beams of one type two letters are used, the first being the series and the second the type of that series. Since three beams of each type were made,

a numeral added to the two letters is used to designate a single beam; that is, AC–1, AC–2, and AC–3 designate the three identical beams of the one type (C) of series A.

TABLE 1.—*Schedule of test beams and types of hollow tile used*

Beams	Hollow tiles			
	Lot No.	Type	Kind of clay	Joints
AA	-----	Concrete beams	No tiles used	
AB	-----	do	do	
AC	1	6-cell, 8 by 12 by 12 inch	Ohio fire clay	Staggered.
AD	4	do	New Jersey fire clay	Do.
AE	8	do	Indiana surface clay	Do.
AF	6	2-cell, 8 by 5 by 12 inch	New Jersey fire clay	
AG	3	6-cell, 8 by 12 by 12 inch	do	
AH	4	do	do	
AI	5	4-cell, 8 by 12 by 12 inch	do	
BA	-----	Concrete beams	No tiles used	
BB	2	3-cell, 6 by 12 by 12 inch	Ohio fire clay	Do.
BC	7	do	New Jersey fire clay	Do.
BD	9	do	Indiana surface clay	Do.
BE	7	do	New Jersey fire clay	Opposite.
BF	5	4-cell, 8 by 12 by 12 inch	do	Staggered.
DA	-----	Concrete beams	No tile used	
DB	3	6-cell, 8 by 12 by 12 inch	New Jersey fire clay	Do.
DC	4	do	do	Do.
DD	5	4-cell, 8 by 12 by 12 inch and 6-cell, 8 by 12 by 12 inch	do	Do.
DE	4		do	Opposite.

The beams of series A and B were tested to produce high shearing stresses. They were heavily reinforced for bending stresses to force failures in shear, the area of the tensile reinforcement being 4.45 per cent of the nominal sectional area of the concrete lying above the mid plane of the bars. In these beams each rib contained, in addition to the tensile renforcement, two ¾-inch diameter round steel bars as compressive reinforcement. Each of the beams of series B contained four ⅜-inch diameter round steel bars as transverse reinforcement in the concrete topping. These bars were similar in size, spacing, and position to the reinforcement for stresses due to shrinkage and changes in temperature which are frequently used in floors of this type.

The beams of series A afford comparisons to determine the effects of the strength of the tiles, their weight, and the number of vertical interior webs on the resistance of the tiles to diagonal tension.

Series B represents specimens of a construction similar to ribbed floors with a concrete topping over tile fillers. The beams were constructed with the topping on the upper surface, but were tested with the topping in tension to simulate conditions at the interior supports of continuous construction. In this series are represented three different arrangements of the tiles and also tiles of three different strengths arranged in the same manner.

The beams of series D contained no compressive reinforcement and were tested to produce high bending stresses. They were heavily reinforced for tension in order to permit the development of high compressive stresses in the concrete and tiles. The tiles for the beams were manufactured at one plant from clay obtained from one source, but the three types used differed in weight and design.

2. CONSTRUCTION

The test beams were built in the laboratories of the Bureau of Standards by labor supplied by the Hollow Building Tile Association working under supervision of members of the bureau staff. The placing of the concrete for series A and B was on one day of each week for three consecutive weeks. Fifteen beams, one of each type, were made in

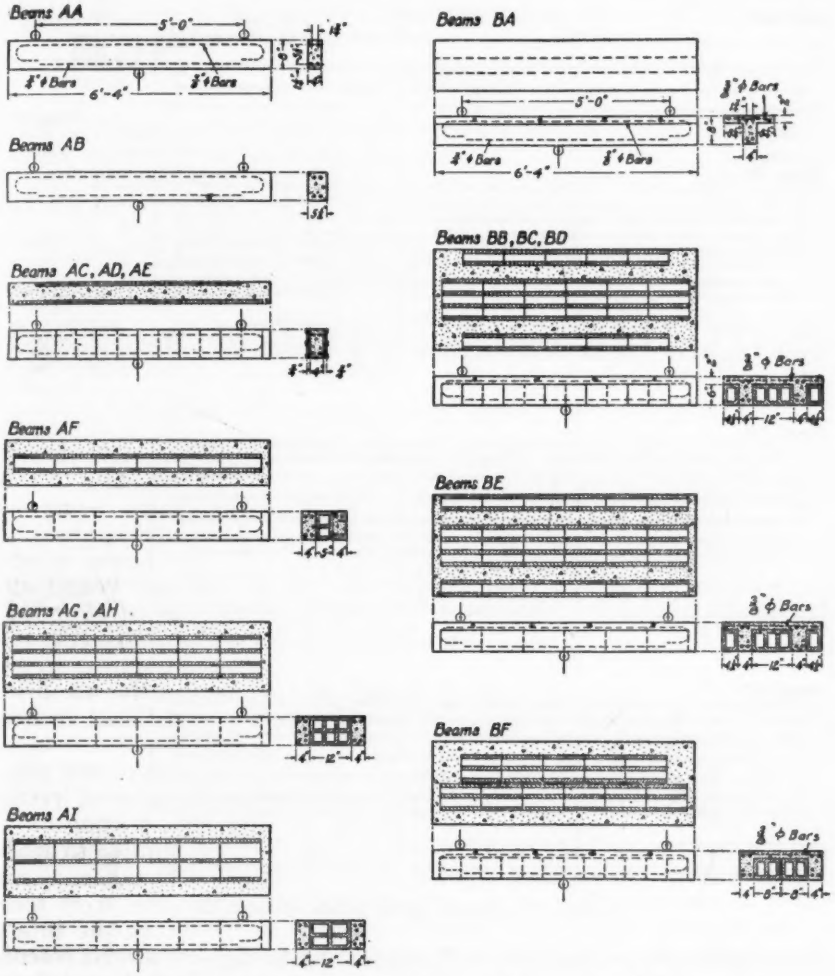

FIGURE 1.—*Details of the beams of series A and B*

one day. Similarly, the beams of series D were made during a period of three weeks, one of each type being cast on each of the three construction days. For example, those designated A–1 and B–1 were made on the same day, and the beams designated A–2 and B–2 were all made on another day.

The construction procedure was the same for the specimens of all series. Wood forms were prepared for the beams built in one day, and the tiles and reinforcement were fixed in position before any con-

crete was placed. In order to prevent concrete from flowing into the cells, the open ends of the tiles were blocked with fragments of broken tiles. The tiles and forms were then thoroughly wetted about one-half hour before and again immediately preceding the pouring of the concrete.

The materials for the concrete were proportioned by weight. After mixing in a drum mixer, the concrete was dumped into a wooden box,

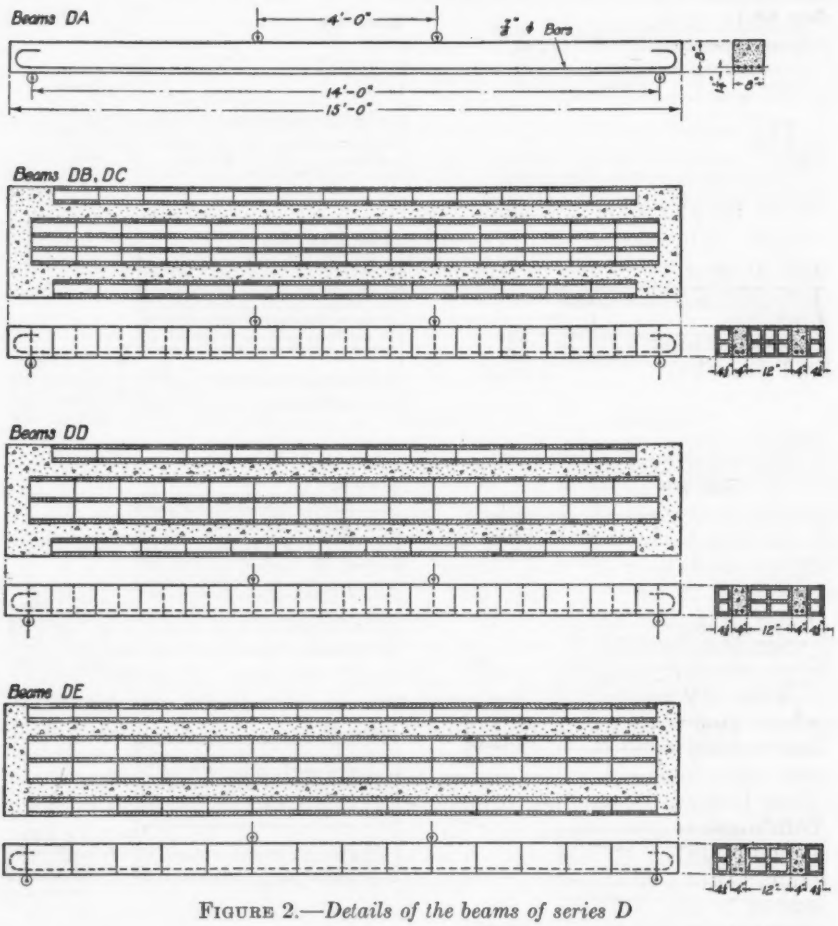

FIGURE 2.—*Details of the beams of series D*

shoveled into wheelbarrows for transporting to the forms, and placed with shovels. Large trowels were used to compact the fresh concrete in the forms, and care was taken to work the concrete around the tiles and reinforcement.

3. STORAGE

Within 2 hours after the concrete was placed, the beams were covered with damp burlap; when 2 days old, they were removed from the forms and placed in piles under burlap kept damp. The beams remained in damp storage until 28 days old and were then permitted to dry in the laboratory for approximately 2 weeks before testing.

III. MATERIALS

1. REINFORCEMENT

The steel reinforcement consisted of round deformed bars. The ⅞-inch bars used as tensile reinforcement conformed to the requirements for "hard" grade and the ¾-inch bars used as compressive reinforcement met the requirements for "intermediate" grade of specification A15–14 of the American Society for Testing Materials.[3] No tests were made on samples of the ⅜-inch diameter bars used as transverse reinforcement in the beams of series B.

2. CONCRETE

The materials for the concrete were purchased locally, and a sufficient quantity for all of the beams was delivered before beginning construction. The cement met the requirements of specification C9–21 for Portland cement of the American Society for Testing Materials. The aggregate consisted of Potomac River sand and gravel similar to the material used locally in building construction except that the gravel was passed through a screen with ¾-inch diameter openings. Gravel of larger size was not used because of the narrow spaces between the bars. The results of sieve analyses of the sand and gravel are given in Table 2.

TABLE 2.—*Sieve analysis and weight of concrete aggregates*

Aggregate	Sieve analysis. Amount retained on each sieve (per cent by weight)								Fineness[1] modulus of aggregates	Weight when dry and rodded
	100	50	30	16	8	4	⅜	¾		
										Lbs./ft.[3]
Sand	96	85	56	41	24	3	0	------	3.05	110
Gravel	100	100	99	99	97	74	13	0	5.82	102
Combined[2]	98	93	80	73	64	41	7	0	4.56	119

[1] Sum of per cents in sieve analysis divided by 100.
[2] Sand and gravel combined in the proportions used in the concrete.

Tests were made to determine the proportion of sand to gravel which yielded the mixture having the greatest density when in a dry and rodded condition. The mixture used contains approximately 10 per cent more gravel than the one giving the maximum density. Trial batches of hand-mixed concrete were made with the aggregates combined in the selected proportions, to determine the amount of cement and water required to make concrete of the desired consistency. For these batches varying amounts of cement and water were added to the sand and gravel; but in each the volume of water equaled the volume of cement. The mix selected for the concrete of the beams consisted of cement and combined sand and gravel in the volume proportions of 1 :3.7. Expressed in terms of the volumes of dry rodded aggregates measured separately, the proportions were 1 :1.84 :2.33, respectively, for the cement, sand, and gravel.

The materials for the concrete of the beams were proportioned by weight. Samples of the sand and gravel were tested for moisture content; and allowances were made, in weighing the aggregate and water, for the moisture in the aggregates. Each batch consisted of 60 pounds of cement, 129 pounds of dry sand, 152 pounds of dry

[3] 1927 Book of A. S. T. M. Standards, Pt. I, p. 132.

gravel, and 44 pounds of water. Of the 44 pounds of water, 4 pounds were allowed for the absorption of the aggregates and the remaining 40 pounds were considered effective in calculating the water-cement ratio. The batches were mixed in a drum mixer for two minutes and then dumped into a box. Samples were then taken for slump tests and for making control cylinders.

Two 6 by 12 inch cylinders were made in steel molds from the concrete of one of the batches for each beam. They were capped with neat cement and removed from the molds within 48 hours, one being stored in the damp room of the concrete laboratory and the other with its corresponding beam. The cylinders stored in the damp room were tested when 28 days old; the others remained with the beams, being kept under damp burlap for 28 days and then in dry storage for 14 days before testing.

The results of the tests of the concrete are given in Table 3. The values, both for slump and for compressive strength, were higher than anticipated from the results of the trial batches of hand-mixed concrete. The average slump from the trial batches was about 7 inches, whereas for the machine-mixed concrete of the same proportions the average slump exceeded 9 inches. The average strength at the age of 7 days of the concrete from hand-mixed batches was 1,050 lbs./in.^{2}; and the strength of 12 cylinders, at the same age, from the machine-mixed concrete for the beams was 1,340 lbs./in.^{2}.[4]

TABLE 3.—*Results of tests of the concrete*

Sample from beams	Slump	Compressive strength at—	
		28 days	42 days
	Inches	*Lbs./in.*^{2}	*Lbs./in.*^{2}
AA	9.1	2,510	3,210
AB	9.4	2,890	3,200
AC	9.5	2,740	3,100
AD	9.0	2,610	3,070
AE	9.5	2,280	2,760
AF	9.1	2,770	3,260
AG	9.3	2,870	3,130
AH	9.4	2,730	3,060
AI	9.0	2,930	3,100
Average	9.3	2,700	3,100
BA	9.4	2,660	2,940
BB	9.6	2,580	2,800
BC	9.0	2,630	2,900
BD	9.0	3,020	3,360
BE	9.4	2,690	3,150
BF	9.5	2,940	3,000
Average	9.3	2,750	3,020
DA	9.6	2,660	3,140
DB	9.4	2,820	3,250
DC	9.4	2,640	2,960
DD	9.3	2,550	2,990
DE	9.8	2,700	3,100
Average	9.6	2,670	3,090

NOTES.—Averages for series A and B (weighted), slump 9.3 inches, strength at 28 days 2,720 lbs./in.^{2}, and strength at 42 days 3,070 lbs./in.^{2}.

Averages for series A, B, and D (weighted), slump 9.4 inches, strength at 28 days 2,710 lbs./in.^{2}, and strength at 42 days 3,070 lbs./in.^{2}.

3. HOLLOW TILES

Nine different lots of hollow tiles were used in the construction of the beams. The types are illustrated in Figure 3 and are listed in Table 4. Two lots were made by a plant in Ohio, five by a plant in New Jersey, and the other two by a plant in Indiana.

[4] Results not included in Table 3.

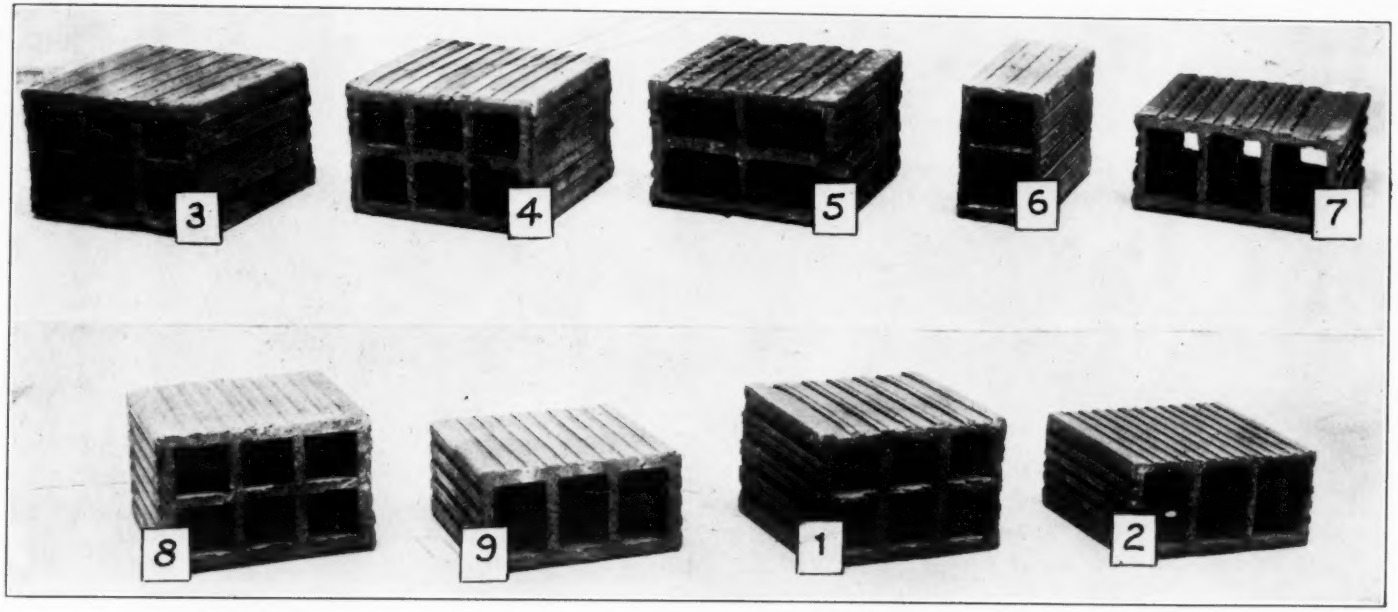

FIGURE 3.—*The hollow tiles*

The numbers refer to the type or lot number.

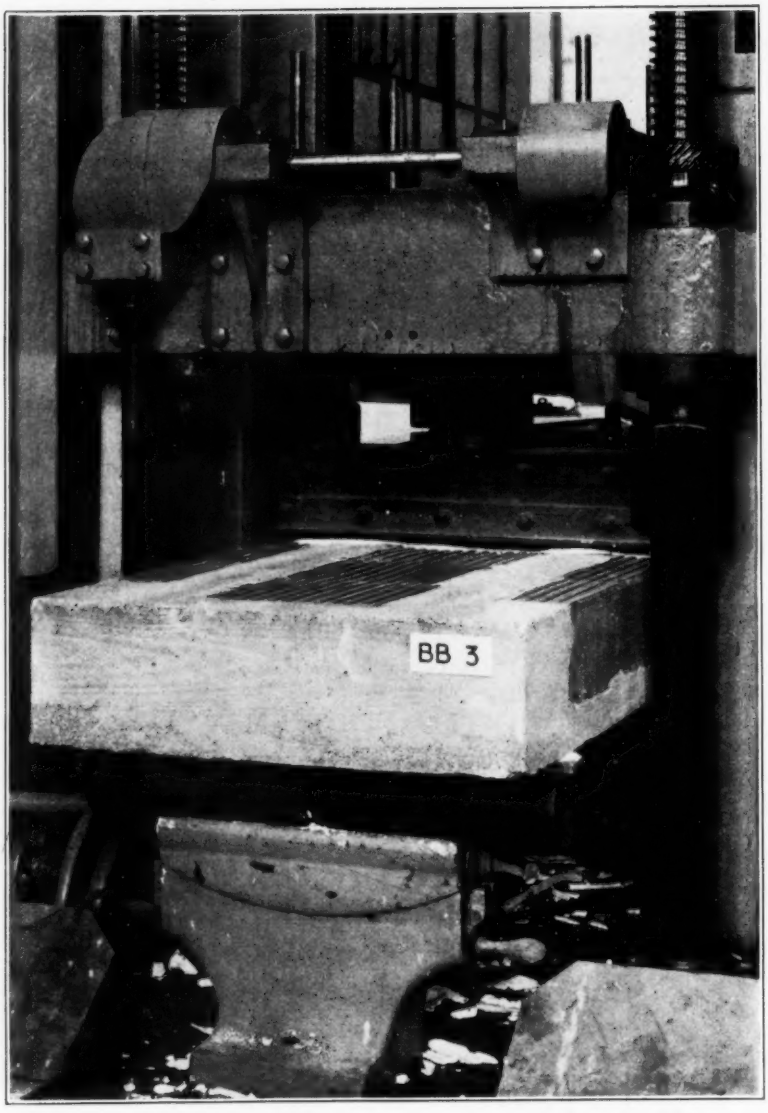

FIGURE 4.—*Beam BB–3 in testing machine for the shear test*

TABLE 4.—*Results of tests of the hollow tiles*

[Each value is the average for 10 tests]

Lot No.	Hollow tiles		Thickness of shells vertical in beams	Weight			Compressive strength		Modulus of elasticity (net area)	Absorption	
	Type	Material		Total	Gross volume	Net volume	Gross area	Net area		24-hour immersion	1-hour boiling
			Inch	*Pounds*	*Lbs./ft.*³	*Lbs./ft.*³	*Lbs./in.*²	*Lbs./in.*²	*Lbs./in.*²	*Per cent*	*Per cent*
1	6-cell, 8 by 12 by 12 inches	Ohio fire clay	0.74	33.1	51.0	125	2,490	6,080	3,460,000	6.1	10.1
1W	do	do	.74	33.0	50.9	125	[1] 2,250	[1] 5,520	[1] 3,440,000	6.4	10.5
2	3-cell, 6 by 12 by 12 inches	do	.60	20.2	43.2	130	2,410	7,230	4,550,000	4.5	7.9
3	6-cell, 8 by 12 by 12 inches	New Jersey fire clay	.94	38.5	57.2	118	1,870	3,860	2,580,000	9.6	14.4
3W	do	do	.94	38.4	56.7	117	[1] 1,750	[1] 3,620	[1] 2,520,000	10.0	14.8
4	do	do	.78	33.9	51.1	118	1,630	3,770	2,890,000	10.3	14.1
5	4-cell, 8 by 12 by 12 inches	do	[2] .83	30.1	44.7	118	1,140	3,020	2,490,000	11.1	14.0
6	2-cell, 8 by 5 by 12 inches	do	.71	15.7	56.0	120	1,870	4,000	3,170,000	9.8	13.6
7	3-cell, 6 by 12 by 12 inches	do	.69	21.0	44.2	124	1,850	5,210	4,050,000	7.0	10.3
8	6-cell, 8 by 12 by 12 inches	Indiana surface clay	.92	31.1	46.4	105	1,250	2,870	1,740,000	22.6	24.1
8W	do	do	.92	30.8	46.0	106	[1] 1,150	[1] 2,680	[1] 1,630,000	22.4	23.9
9	3-cell, 8 by 12 by 12 inches	do	.80	21.4	43.7	108	1,730	4,260	1,930,000	20.9	22.3

[1] Tested when wet, after 24 hours immersion in water at 70° F.

[2] In beams BF, thickness was 0.76 inch.

Ten tiles of each lot were selected by appearance to cover the range in burning for the customary physical tests of the individual tiles. In so far as applicable, the methods described in specification C34–27 [5] of the American Society for Testing Materials were followed in conducting these tests. For the compressive tests, the tiles were loaded parallel to the direction of the cells. The results of the tests are given in Table 4. In addition to the 10 tiles of each lot tested in the dry condition, 10 samples of each of lots 1, 3, and 8 were tested for compressive strength and modulus of elasticity immediately after being immersed in water at room temperature for 24 hours. These auxiliary tests of saturated tiles were made to determine the effect of moisture on their strength and stiffness, since the tiles in the beams probably were not completely dry at the time of test. The results indicate that the presence of moisture in the tiles did not greatly lessen their strength; in no case was the reduction in strength greater than 10 per cent. The slight reduction in strength indicated by the values in Table 4 probably is somewhat greater than the true values, since the strength of both gypsum and cement, of which the capping materials were composed, is known to be reduced by the presence of moisture.

IV. METHOD OF TESTING BEAMS

1. SHEAR TESTS OF SERIES A AND B

The position of the beams in the forms was the same as shown in Figures 1 and 2; those of series D were tested in the same position, while, for convenience in applying the loads, those of series A and B were inverted before testing. It was desired that the beams of series A and B represent portions of slabs in regions of negative bending moment. These beams were accordingly built and loaded to cause the surfaces which were uppermost when constructed to be in tension during the tests.

All of the beams were tested in a vertical screw universal testing machine having a capacity of 600,000 pounds. As indicated in Figures 1 and 2, the beams of series A and B were supported over a span of 5 feet spaced symmetrically about the center of the beams and the loads applied at mid span, while those of series D were supported over a span of 14 feet and loaded along two lines, each being 2 feet from mid span. The type of supports and methods of transmitting the loads to the beams are illustrated by the photographs of beams BB–3 and DD–2 shown in Figures 4 and 5.

For the tests of series A and B, the machine was run continuously so as to cause a lowering of the moving (upper) head at the rate of 0.04 inch per minute from the time a test was started until its completion. As the loading progressed, records were kept describing the development of cracks and of the loads at the time each new crack appeared. Each test was stopped when the magnitude of the load and the appearance of the beam indicated that the maximum load had been passed.

[5] 1927 Book of Am. Soc. Test. Mats. Standards Pt. II, p. 213.

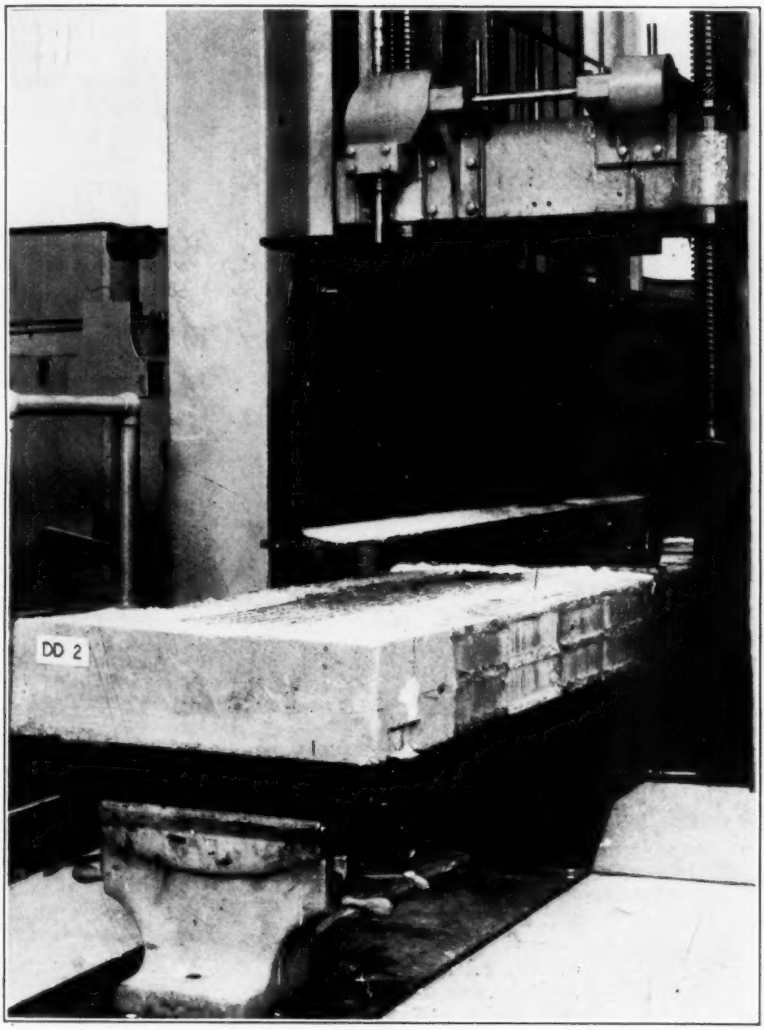

FIGURE 5.—*Beam DD–2 in testing machine for the bend test*

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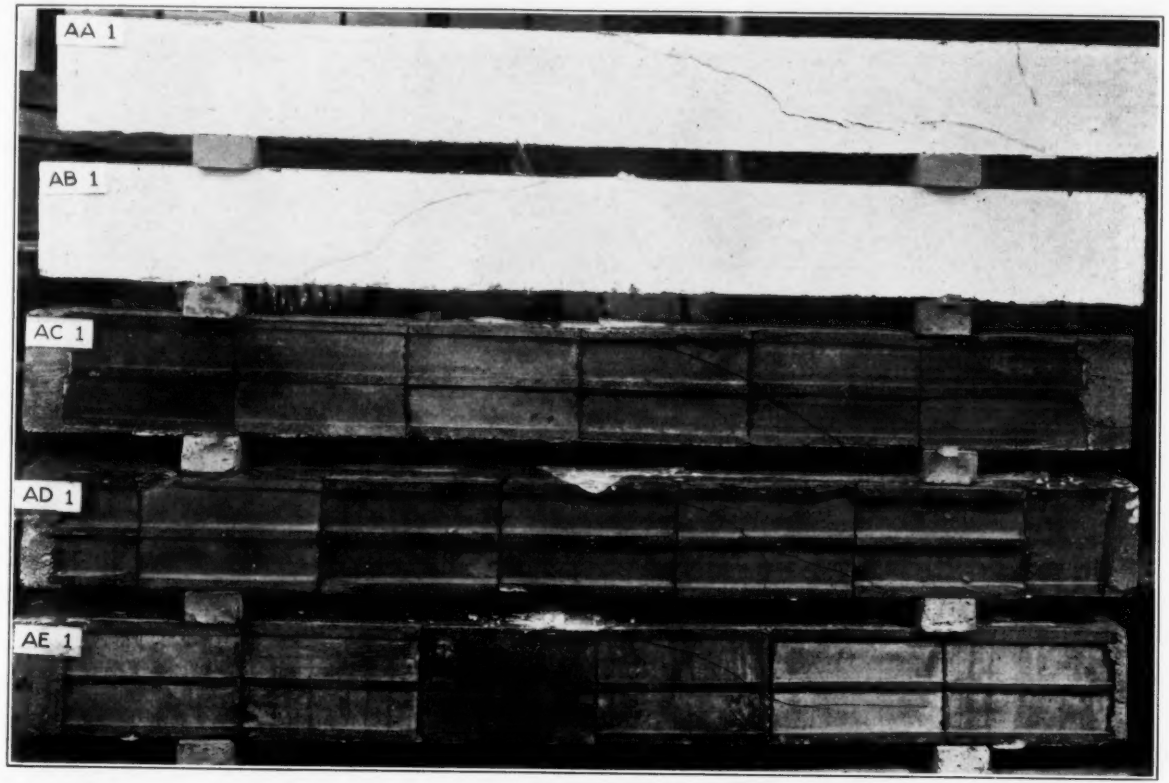

FIGURE 6.—*Typical beams of series A after testing*

FIGURE 7.—*Typical beams of series A and B after testing*

FIGURE 8.—*Typical beams of series B after testing*

2. BEND TESTS OF SERIES D

With series D, measurements were made of the deflections of the beams and of the strains in the concrete, steel, and tiles. The deflections were measured at mid span of the beams on mirror scales, graduated to 0.1 inch, by means of a fine wire fastened to the beams directly over the supports and kept taut with rubber bands. Tensile longitudinal deformations in the steel and compressive longitudinal deformations in the concrete and tiles were measured by strain gages over 8-inch gage lengths located approximately at mid span. There were two gage lines in the reinforcement of each beam, one in each of the two outer bars. One gage line was located on the upper surface of each concrete rib, while those in the tiles were on the upper surfaces, one being above each of the vertical webs and shells.

In making a test a set of observations was made before applying load, and then other sets were made after each 2,000-pound increase in the load until the measurements indicated that either the steel or the concrete had begun to yield appreciably with a constant load on the beam. In most cases the readings were continued to within 10 per cent of the maximum loads. The instruments were then removed, and the machine run continuously until the maximum load had been passed.

V. RESULTS OF THE SHEAR TESTS, BEAMS OF SERIES A AND B

1. CRACKS AND FAILURES

The failures of all of the beams of series A and B were accompanied by the appearance of diagonal cracks extending from the lower portion of the beam near a support toward the upper surface at mid span. The diagonal cracks in the tiles were approximately in the same plane and of about the same length as the cracks in the concrete of contiguous ribs. Photographs of the beams taken after test are shown in Figures 6, 7, and 8.

In the beams without a topping over the tiles (series A) no diagonal cracks were evident until the maximum load was reached. The failure of each of these beams was sudden and occurred simultaneously with the formation of a diagonal crack in one end of a beam.

In some of the beams with a topping over the tiles (series B) diagonal cracks became visible before the maximum load had been reached. The first diagonal cracks in these beams were noted at loads ranging from 66 to 100 per cent of the maximum. On the average, the first crack appeared at a load of 94 per cent of the maximum.

The results of the tests are given in Table 5. All computed quantities were calculated by the methods used in common practice, the beam formulas employed being those given in the 1924 report of the Joint Committee on Standard Specifications for Concrete and Reinforced Concrete.[6] For these calculations a value of 12 for the ratio (n) of the modulus of elasticity of the steel to that of the concrete was assumed.

[6] Proc. Am. Soc. for Test. Mats., **XXIV** Pt. I, p. 313; 1924. Also published in the proceedings of other technical organizations and reprinted in books on concrete construction.

TABLE 5.—*Series A and B, dimensions of beams and results of tests*

Depth to tensile reinforcement ..... d=6.8 inches.
Depth to compressive reinforcement ..... d'=1.3 inches.
Area of tensile reinforcement in each rib ..... A_s=1.20 square inches.
Area of compressive reinforcement in each rib ..... A_s'=0.88 square inch.

A, CONCRETE BEAMS (SERIES A AND B)

Beam No.	Width of concrete rib b	j	Maximum load W	Maximum shearing stress $v=\frac{V}{bjd}$
	Inches		*Pounds*	*Lbs/in.²*
AA-1	4.20	0.820	9,200	196
AA-2	4.25	.820	8,750	185
AA-3	4.68	.822	8,600	164
Average				182
AB-1	5.60	.827	11,600	184
AB-2	5.85	.828	11,500	175
AB-3	5.85	.828	12,850	195
Average				185
BA-1	4.00	.819	9,000	202
BA-2	3.90	.818	9,250	213
BA-3	3.98	.819	9,750	220
Average				212

B, COMBINATION BEAMS WITHOUT A TOPPING (SERIES A) (j ASSUMED AS 0.83)

Beam No.	Lot No. of tile in beam	Total width of beam	Total width of concrete ribs	Maximum load W	Width of concrete web equivalent in shearing strength	Width of concrete web equivalent to 1 inch of tile shell
		Inches	*Inches*	*Pounds*	*Inches*	*Inches*
AC-1	1	5.47	3.99	12,000	5.79	1.22
AC-2	1	5.62	4.14	13,900	6.71	1.74
AC-3	1	5.65	4.17	12,750	6.15	1.34
Average						1.43
AD-1	4	5.78	4.22	11,800	5.70	.95
AD-2	4	6.02	4.46	13,300	6.42	1.26
AD-3	4	5.70	4.14	13,000	6.28	1.37
Average						1.19
AE-1	8	5.75	3.93	12,000	5.79	1.02
AE-2	8	5.90	4.08	13,250	6.40	1.27
AE-3	8	5.90	4.08	10,650	5.14	.58
Average						.96
AF-1	6	13.00	7.89	19,000	9.17	.91
AF-2	6	13.10	7.99	21,750	10.50	1.77
AF-3	6	13.15	8.04	20,600	9.96	1.35
Average						1.34
AG-1	3	20.00	7.84	19,000	9.17	.71
AG-2	3	20.05	7.89	21,800	10.52	1.40
AG-3	3	20.08	7.92	20,650	9.97	1.09
Average						1.07
AH-1	4	20.10	7.99	18,700	9.03	.67
AH-2	4	20.15	8.04	20,200	9.75	1.10
AH-3	4	20.18	8.07	19,700	9.51	.92
Average						.90
AI-1	5	20.22	8.09	20,800	10.04	1.18
AI-2	5	20.20	8.07	22,600	10.91	1.71
AI-3	5	20.30	8.17	22,150	10.69	1.52
Average						1.47

TABLE 5.—*Series A and B, dimensions of beams and results of tests*—Continued

C, COMBINATION BEAMS WITH A TOPPING (SERIES B) (J ASSUMED AS 0.83)

Beam No.	Lot No. of tile in beam	Total width of beam	Total width of concrete ribs	Maximum load W	Width of concrete web equivalent in shearing strength	Width of concrete web equivalent to 1 inch of tile shell
		Inches	*Inches*	*Pounds*	*Inches*	*Inches*
BB-1	2	28.45	8.09	29,650	12.40	1.80
BB-2	2	28.70	8.34	34,450	14.40	2.52
BB-3	2	28.90	8.54	30,600	12.79	1.77
Average						2.03
BC-1	7	29.20	8.59	29,200	12.21	1.31
BC-2	7	29.05	8.44	30,400	12.71	1.55
BC-3	7	28.88	8.27	30,700	12.83	1.65
Average						1.50
BD-1	9	28.85	8.13	27,750	11.59	1.07
BD-2	9	28.90	8.18	28,600	11.95	1.17
BD-3	9	28.40	7.68	24,900	10.41	.85
Average						1.03
BE-1	7	29.00	8.39	29,600	12.37	1.44
BE-2	7	29.28	8.67	29,300	12.24	1.29
BE-3	7	29.15	8.54	30,050	12.56	1.46
Average						1.40
BF-1	5	24.00	7.75	23,550	9.84	1.38
BF-2	5	24.15	8.00	23,450	9.80	1.18
BF-3	5	24.25	8.10	22,800	9.53	.95
Average						1.17

Each rib of the beams of series A and B contained two ⅞-inch round bars as tensile reinforcement and two ¾-inch round bars as compressive reinforcement. Measurements indicated that the depth of the beams from the extreme fiber in compression to the center of the compressive reinforcement was 1.3 inches within ± 0.1 inch and to the center of the tensile reinforcement was, within the same limits, 6.8 inches.

2. METHOD OF COMPUTING AND TABULATING RESULTS

The strengths of the concrete beams AA and AB are taken as a measure of the strength of the concrete ribs of the combination beams of series A. Similarly, the strength of the concrete beams BA serve as a measure of the strength of the concrete portions of the other beams of series B. Owing to differences in the dimensions of the beams and the tiles, the maximum loads supported by the beams are not direct measures of the value of 1 unit width (or thickness) of tile in increasing the strength of the combination beams. A convenient method of making an allowance, in design, for the additional strength given by the tiles is to consider that their effect is equivalent to an increase in the widths of the concrete ribs. In Tables 5, B and 5, C are given the widths of concrete webs equivalent to 1 inch of tile shells for each of the combination beams. The following examples illustrate the method of calculating these widths from the test data.

In series A there were two sets (AA and AB) of concrete beams, the beams of each set being, except for width, of identical design. Beams AA had approximately the same width as the concrete ribs of combination beams. Beams AB having a greater width, were included to determine whether there would be an appreciable difference in maximum shearing stress due solely to an increase in the width of the beam. Since the maximum shearing stresses (Table 5, A) were about the same for the two sets, the average strength of the six beams (AA and AB) was taken as a measure of the resistance of the concrete ribs of the combination beams of series A. Using this average value (184 lbs./in.^{2}) for the resistance of the concrete to shearing stress, the widths of rectangular concrete beams of the same depth required to resist the loads supported by each of the combination beams of series A were computed by the following formula:

$$b = \frac{W}{2vjd}$$

where

W = the maximum load, pounds, supported by a combination beam.
v = 184 lbs./in.^{2}, the average maximum shearing stress for the concrete beams AA and AB.
j = taken as 0.83 for all combination beams.[7]
d = 6.8 inches.

These widths may be considered as the widths of concrete beams equivalent in resisting shear to a corresponding tile and concrete beam. Deducting from the width b the total width of the concrete in a beam gives the width of concrete equivalent to the effect of the tile in increasing the shearing resistance of the beam. These values expressed in terms of the total thickness of the vertical tile shells, having a bond contact with the concrete, are given in Table 5, B.

For the beams of series B, the values of the tiles in increasing the shearing resistance of the beams were calculated in the same manner, the only difference being that the shearing stress (v) was taken as 212 lbs./in.^{2}, the average for beams BA.

3. RELATIVE VALUE OF THE SHELLS AND THE INTERIOR WEBS OF THE TILES IN RESISTING SHEAR

The results from the tests of beams AF, AG, AH, and AI may be compared to determine the effect of the number of cells in the tiles on their value in resisting shear. In beams AF there were no vertical interior webs, in beams AI there was one, and in beams AG and AH there were two. The tiles for these beams were manufactured by one plant and from one source of material, and there was not a large difference in the strength of the material. The values given in Table 5, B indicate that there was no relation between the effectiveness of the tiles and the number of cells. It is seen also that, on the average, the value of the tiles in these beams was about the same as for beams

[7] Because of the effect of the tiles, the values of j (ratio of lever arm of resisting couple to the depth d) for the combination beams differed somewhat from those based upon the concrete section only of the beams. Since the amount of this difference is not known, and since relatively large changes in the effective widths are required to produce important changes in the values of j, a constant value (j=0.83) was used in the calculations pertaining to the combination beams of series A and B.

AD having only shells of tiles manufactured by the same plant. It may be concluded, therefore, that the interior webs of the tiles were of little if any value in increasing the resistance of the beams to shear and that the resistance of the tiles was due almost entirely to the vertical shells bonded to the concrete ribs.

4. EFFECT OF THE STRENGTH, MODULUS OF ELASTICITY, AND ABSORPTION OF THE TILES

In series A the beams AC, AD, and AE were of identical design except for the quality of the tiles; the results for these beams may be compared, therefore, to determine the effect of the physical properties of the tiles on their values in increasing the strength of the beams. A comparison between the compressive strengths of the tiles and the widths of concrete equivalent in shear to each inch width of tile shells in these beams is shown by the filled circles in Figure 9. The

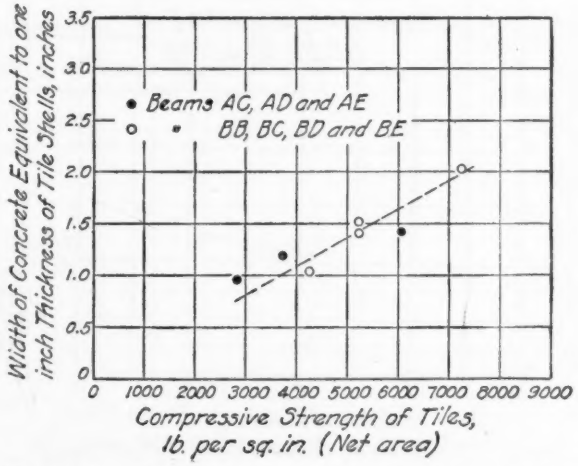

FIGURE 9.—*Relation between the compressive strength of the tiles and their value (per unit thickness of shells) in resisting shear in the beams*

results for the beams BB, BC, and BD, which were identical except for the tiles, are shown by the open circles in the same figure.

The results shown in Figure 9 indicate that, in general, the assistance of the tiles increased with an increase in the compressive strength of the tiles. With tiles having a compressive strength greater than the average strength of the concrete cylinders (3,070 lbs./in.^{2}), the effect of the tiles in resisting shear was equivalent to an increase in the widths of the concrete webs greater than the thickness of the tile shells in contact with the concrete.

The strength of the beams of series B was on the average greater per unit of width of the concrete ribs than for the beams of series A. With the value of the tiles expressed in terms of the strength of the concrete beams, it is seen from Figure 9, however, that there was not a great difference between the assistance of the tiles in the two series; that is, although the maximum shearing stress for beams BA was greater than for beams AA and AB, the effect of the tiles in the beams

with a topping was also somewhat greater than without the topping; and the results indicate that the value of the tiles in increasing the resistance of the beams to shear was about the same in the two types of construction when expressed in terms of equivalent widths of concrete.

Figure 10 shows a comparison between the modulus of elasticity of the tiles and their value in resisting shear. Though the points are somewhat scattered, their positions indicate a general increase in shearing resistance with an increase in the modulus of elasticity of the tiles.

In Figure 11 is shown a graphic comparison between the absorption of the tiles and their value in resisting shear in the beams. The points in this diagram seem to follow a line of single curvature more closely than in either of the two preceding.

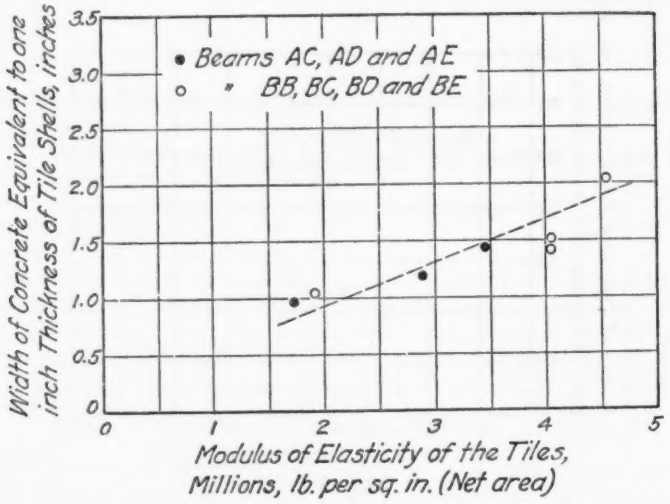

FIGURE 10.—*Relation between the modulus of elasticity of the tiles and their value (per unit thickness of shells) in resisting shear in the beams*

Similar relations could be shown between the value of the tiles and different combinations of their physical properties. In particular, there seemed to be for these data a close relation between the product of the strength and modulus of elasticity of the tiles and their resistance to shear when expressed as in Figures 9, 10, and 11. Since, however, more data would be needed to establish any definite relation which may exist for tiles in general, the classification of floor tiles on the basis of compressive strength may be justified on the grounds that such a basis is simple to apply and seems reasonable.

5. EFFECT OF THE POSITION OF THE JOINTS IN ALTERNATE ROWS OF THE TILES

Beams BC and BE were of identical construction except for the position of the joints between the tiles. In beams BC the joints between the tiles of alternate rows were staggered, while in beams

BE they were opposite. (See fig. 1.) Although the value of the tiles in the beams with staggered joints was slightly greater, the difference was small in comparison to differences in the strengths of beams of the same type of construction; and the results indicate that the position of the joints in alternate rows of tiles does not have an important effect on the assistance of the tiles in resisting shear.

6. EFFECT OF INCREASING THE NUMBER OF ROWS OF TILE BETWEEN THE CONCRETE RIBS

The type of construction represented by beams BF differed from that of the other beams in having two (instead of one) rows of tile between the concrete ribs. The strengths of these beams were not far different from the strengths of those containing only one row of tiles, but otherwise similar. By comparing the value of the tiles in beams BF with their value in the other beams (given in Table 5 and

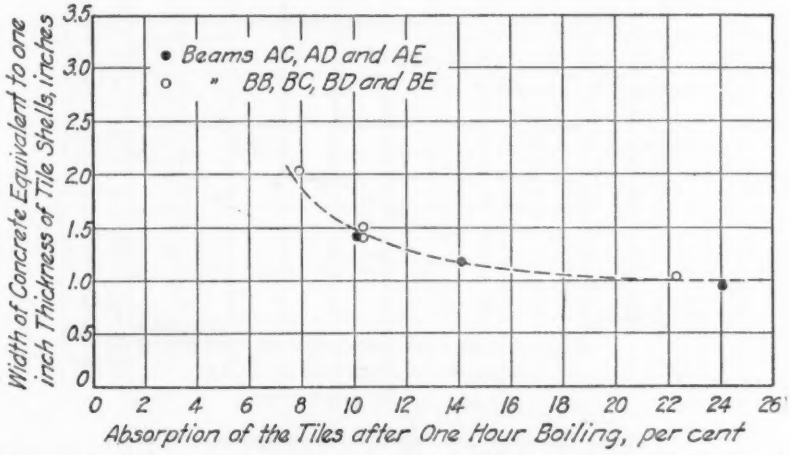
Width of Concrete Equivalent to one inch Thickness of Tile Shells, inches
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
• Beams AC, AD and AE
○ " BB, BC, BD and BE
0 2 4 6 8 10 12 14 16 18 20 22 24 26
Absorption of the Tiles after One Hour Boiling, per cent

FIGURE 11.—*Relation between the absorption of the tiles and their value (per unit thickness of shells) in resisting shear in the beams*

figs. 9, 10, and 11), it is seen that an increase in the number of vertical shells and webs in beams BF ,which were not in contact with the concrete ribs, did not increase the strength appreciably. It is seen, further, that the shearing resistance of the tiles in these beams was about the same per unit of width of the shells in contact with the concrete as in other beams containingg tiles of about the same physical properties.

VI. SUMMARY OF DATA ON SHEAR TESTS OF HOLLOW TILE AND CONCRETE BEAMS

1. COMPARISONS BETWEEN THE RESULTS OF THE 1924 AND 1926 SERIES

The results of both the 1924[8] and the 1926 series indicate that the tiles assisted materially in resisting shear. A direct quantitative comparison between the values for the tiles in the two series, however,

[8] Reported in B. S. Tech. Paper No. 291.

must be somewhat uncertain because of differences in the types of specimens and the methods of testing. There is further uncertainty because some of the beams of the first series did not fail by diagonal tension.

Differences in the values for the two series, due to differences in the manner of loading and in the forms of the specimens, probably may be taken account of by comparing the strengths of the concrete beams of the same series which were similar in total dimensions and in reinforcement to the concrete ribs of the combination beams. Then, using the method described in Section V, 2, the widths of concrete equivalent, in resisting shear, to 1 inch thickness of tile shells may be found for each combination beam. Similar quantities for the 1926 series are given in Table 5 and in Figures 9, 10, and 11. For the 1924 series these widths were calculated only for the combina-

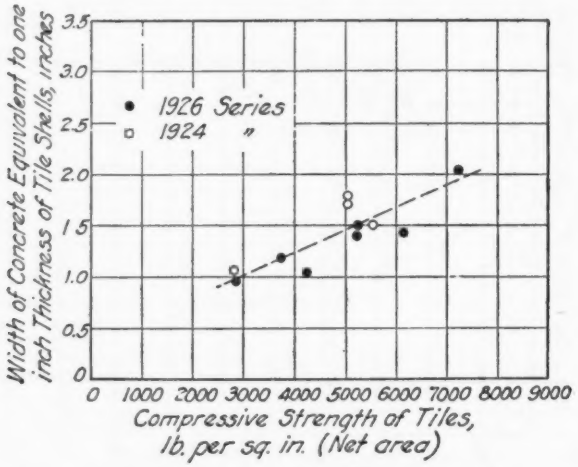

FIGURE 12.—*Relation between the compressive strength of the tiles and their value (per unit thickness of shells) in resisting shear in the beams, including results of tests made in 1924*

tion beams without a topping which were loaded in the same manner as the concrete beam B of that series.

These results for the two series are shown in Figures 12, 13, and 14. The values for the tiles when expressed in terms of equivalent widths of concrete are not widely different for the two series. There are reasons for believing, however, that the close proximity of the points for the two series is due to the combination of two influences, not yet considered in detail.

Since the values for the tiles are expressed in terms of equivalent widths of concrete, a difference in the strengths of the concrete for the two series would be expected to cause a change in the values; that is, the stronger the concrete the less width required to be equivalent to a given tile shell. Taking into consideration the proportions of the materials and curing conditions it seems safe to conclude that the concrete in the beams of the 1926 series was stronger than that in the earlier series. This influence would tend to cause the points for the 1924 series in Figures 12, 13, and 14 to lie above the

others. Some of the beams of the earlier series, however, failed in tension or in compression before they had developed their full strength in shear; and, therefore, the points lie below the positions they otherwise would occupy. It seems then that, although the widths of concrete equivalent to the tile shells in the 1924 series were about the same as in the later series, they would have been larger, owing to the difference in the strength of concrete, if the beams had been strong enough in bending to develop their full strength in shear in the tests. The data, therefore, agree with the expectation that the values of the tiles, expressed in terms of equivalent widths of concrete, would become less with an increase in the strength of the concrete.

Perhaps the chief value to be derived from the comparison between the results of the two series is the knowledge that the tiles appreciably increased the shearing strength of the beams which differed in the

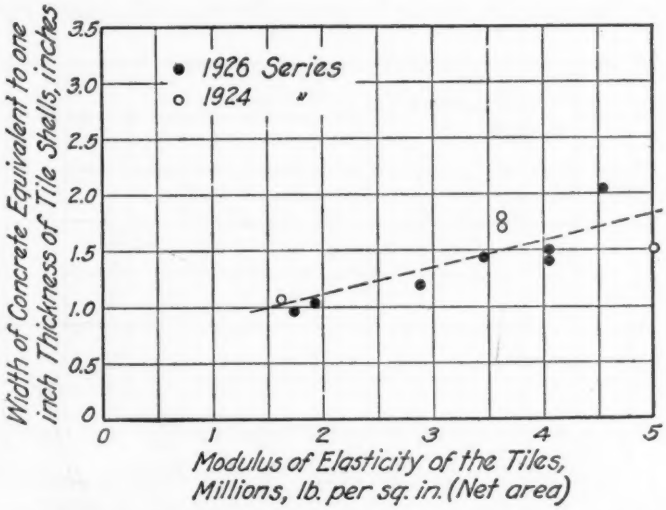

FIGURE 13.—*Relation between the modulus of elasticity of the tiles and their value (per unit thickness of shells) in resisting shear in the beams, including results of tests made in 1924*

materials used, their construction, methods of fabrication and curing. As previously noted, the specimens for the 1924 series were made by a contractor who followed methods commonly used in the construction of buildings. Those of the 1926 series were carefully made in the laboratory; the concrete was uniformly of high strength and was carefully placed so as to compact the concrete and insure its contact with the reinforcement and tiles. The fact that the tiles were effective under such widely different conditions gives confidence that the results may be applied to design.

2. APPLICATION OF RESULTS TO DESIGN

Although a discussion of working stresses and factors of safety is beyond the scope of this paper, it may be worth while to mention certain possible simplifications in the application of the results to the design of hollow tile and concrete slabs, that are not apparent from the data of the tests alone.

Usually the strength of the concrete and the physical properties of the tiles will not be known to the designer of a hollow tile and concrete slab. In general, the strength calculations for a slab will be based in part upon the assumptions: (1) The strength of the concrete will exceed a given amount, and (2) the tiles will conform to certain minimum requirements for weight and strength. In view of this it usually would not be practicable to vary the allowance for the tiles in accordance with small changes in the physical properties of the materials used in the construction. Consequently, a practical method of making an allowance for the tiles in design would be to consider the width of the section effective in resisting shear or diagonal tension equal to the width of the concrete web plus an arbitrary amount which would be the same for all tiles meeting the minimum requirements of the specification in use.

It would seem at first thought that such a rule would be grossly unjust in that all tiles would be given the same allowance regardless

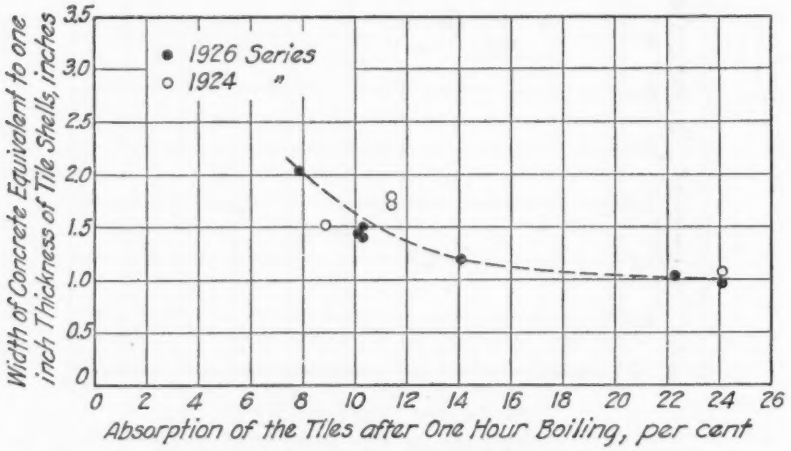

FIGURE 14.—*Relation between the absorption of the tiles and their value (per unit thickness of shells) in resisting shear in the beams, including results of tests made in 1924*

of their quality; that is, the allowance might be unduly small for tiles of medium or hard classes, and, perhaps, too large for tiles of the soft class. However, for tiles of the same size, design, and weight those classed as soft usually have thicker shells than those of the harder classes. Hence, the effect of the difference in strength on their value in resisting shear is not large, the increased shell thickness of the soft tiles compensating in part for their weaker structure. This can not be reduced to a mathematical statement because there is not a close relation between the compressive strength (net area) of hollow tile and the density of the material. There is, however, a decided tendency for a dense material to give a high strength and a low absorption (and vice versa), and Foster shows a close relation between bulk density and absorption.[9]

[9] J. Am. Ceram. Soc., **7**, No. 3; March, 1924; and Proc. Am. Soc. Test. Mats., **XXIV**, Pt. I, p. 411; 1924.

The widths of concrete equivalent in resisting shear to one row of tiles in the beams are shown in Figure 15. By comparing these values with those in Figure 9, it is seen that, while the resistance of the tiles per unit of thickness of the tile shells (fig. 9) is rather closely related to the compressive strength, the resistance of one row of tiles (fig. 15) is not greatly affected by small differences in the compressive strength. This difference is due to the fact that the tiles made of stronger material usually had thinner shells.

The results of the beam tests indicated that with tiles ranging in compressive strength (net area) from 2,870 to 7,230 lbs./in.^{2}, one row was equivalent in resisting shear to concrete webs from 1.6 to 2.4 inches in width, 6 out of the 7 values shown in Figure 15 lying between 1.6 and 2.1 inches. These values indicate that only a rough estimate of the compressive strength of the tiles is needed for making a

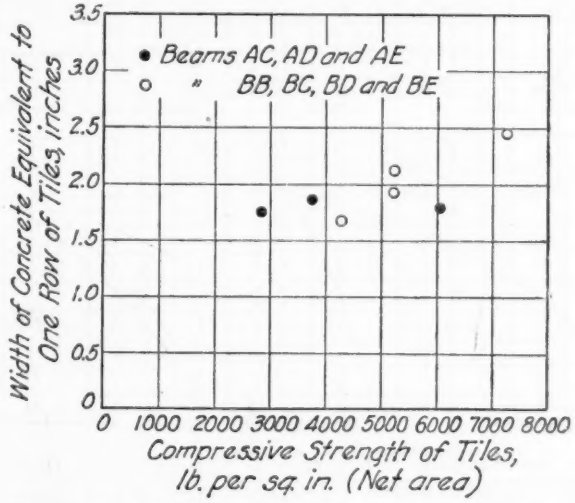

FIGURE 15.—*Relation between the compressive strength of the tiles and the value of one row in resisting shear in the beams*

fair allowance for their assistance, provided the tiles are similar in designs and weights to those tested. In selecting the allowance for tiles, the strength of the concrete should be given consideration. The values for the tiles just given were obtained with concrete, of which cylinders developed a compressive strength of 3,000 lbs./in.^{2}. As previously noted, smaller values would be expected with concrete of greater strength and larger values with concrete of lesser strength.

VII. RESULTS OF THE BEND TESTS, BEAMS OF SERIES D

1. TYPES OF FAILURES

Two of the concrete beams (DA–1 and DA–2) failed by the crushing of the concrete; and, although the third beam (DA–3) failed by diagonal tension, the measured strains in the concrete indicate that a compressive failure would have taken place with an increase in the

maximum load of not more than 5 per cent. With the exception of beams DD–2 and DE–3, all of the combination beams of series D failed in compression. For these two, the steel reinforcement had begun to yield before the maximum load had been reached.

Even though the maximum loads supported by the combination beams were about equal in many cases to the loads resisted by the concrete beams, it is seen by the graphs of Figures 16, 17, and 18 that the deformations in the concrete and reinforcement of the

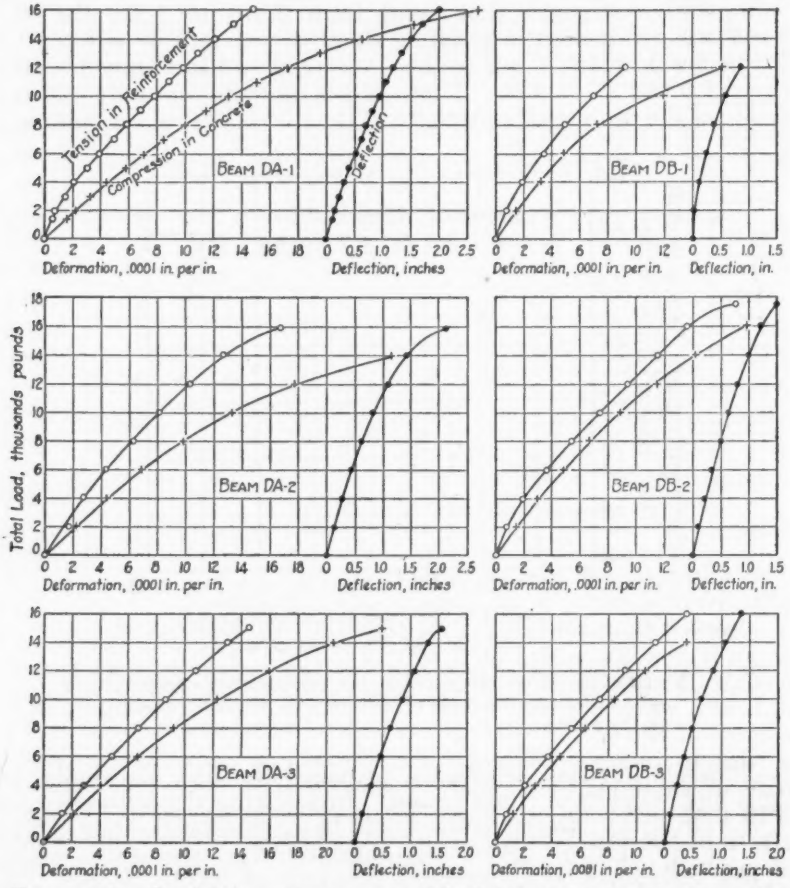

FIGURE 16.—*Load-deformation curves and load-deflection curves for beams DA and DB*

The elongations in the lower surface of the reinforcement are shown by open circles, the compressions in the upper surface of the concrete by crosses, and the deflections of the beams by filled circles.

combination beams and the deflection of these beams were markedly less than the similar values for the concrete beams. For example, the strains in the concrete and steel and the deflections of the combination beams corresponding to a load of 8,000 pounds were on the average, respectively, 70, 84, and 74 per cent of the similar values for the concrete beams. It is apparent from these values and from the curves of Figures 16, 17, and 18 that the tiles were effective in stiffening the beams.

TABLE 6.—*Series D, dimensions of beams and results of tests*

Beam No.	Lot No. of tiles in beams	Total width of tile shells in contact with concrete ribs t	Depth to steel d	Total width of concrete ribs b	Approximate load at partial failure of bond to tile	Maximum load L	Computed maximum compressive stress f_c	Type of failure
		Inches	*Inches*	*Inches*	*Pounds*	*Pounds*	*Lbs./in.²*	
DA-1	(1)	----	7.06	8.23	----	16,000	4,775	Compressive.
DA-2	(1)	----	7.14	8.23	----	15,850	4,635	Do.
DA-3	(1)	----	6.98	8.23	----	15,500	4,720	Diagonal tension.
Average	----	----	7.06	8.23	----	15,783	4,710	
DB-1	3	3.76	6.78	7.82	11,000	12,000	4,010	Compressive.
DB-2	3	3.76	6.82	7.85	16,000	17,450	5,755	Do.
DB-3	3	3.76	6.78	7.63	14,000	16,000	5,460	Do.
Average	----	3.76	6.79	7.77	14,000	15,150	5,075	
DC-1	4	3.12	6.72	7.96	12,000	15,350	5,140	Do.
DC-2	4	3.12	6.73	8.01	12,000	16,500	5,485	Do.
DC-3	4	3.12	6.78	7.96	14,000	16,000	5,275	Do.
Average	----	3.12	6.74	7.98	12,667	15,950	5,300	
DD-1	5, 4	3.32	6.63	8.01	14,000	17,100	5,840	Do.
DD-2	5, 4	3.32	6.68	7.81	14,000	16,950	5,830	Tensile or compressive.
DD-3	5, 4	3.32	6.63	7.98	14,000	16,700	5,720	Compressive.
Average	----	3.32	6.65	7.93	14,000	16,917	5,797	
DE-1	5, 4	3.32	6.71	7.91	12,000	17,950	6,060	Do.
DE-2	5, 4	3.32	6.73	7.98	15,000	16,000	5,335	Do.
DE-3	5, 4	3.32	6.81	8.01	14,000	17,350	5,645	Tensile.
Average	----	3.32	6.75	7.97	13,000	17,100	5,680	

[1] No tiles.

The effectiveness of the tiles at moderate loads was indicated qualitatively also by the measured deformations in the tiles; but it was observed that, in general, the strains in the tiles did not increase with an increase in load throughout the entire range of loading. On the contrary, the bond between the concrete and tiles in all combination beams was partially broken before reaching the maximum loads. For most of the beams the bond was sufficient to cause the strains in the tiles to increase with an increase in load until the measured strains in the upper surfaces of the concrete ribs were from 0.0010 to 0.0018 inch per inch, whereas the compressive strains in the upper surfaces of the concrete beams were in all cases greater than 0.0024 inch per inch before the maximum loads were reached. Although the final failures of the combination beams may be attributed to bending stresses, the partial failures of the bond between the concrete and tiles had occurred at loads less than the maximum, and the tiles were not as effective then as for the lower loads. In Table 6 are given the approximate loads at which the measured strains in one or more of the gage lines in the tile shells had ceased to increase with an increase in the loads.

2. STRENGTHS OF THE BEAMS

The tests of the beams of series D were planned to obtain information on the value of the tiles in increasing the resistance of the beams

to bending and to compare the strengths of beams which were similar except in either the design or the position of the tiles. Owing to the fact that the tiles had partially broken away from the concrete before bending failures had occurred, the desired comparisons can not be made from the results of the tests unless it can be assumed that the failure of the bond between the concrete and tiles is a typical phenomenon for tile and concrete beams of this type. It is believed, however,

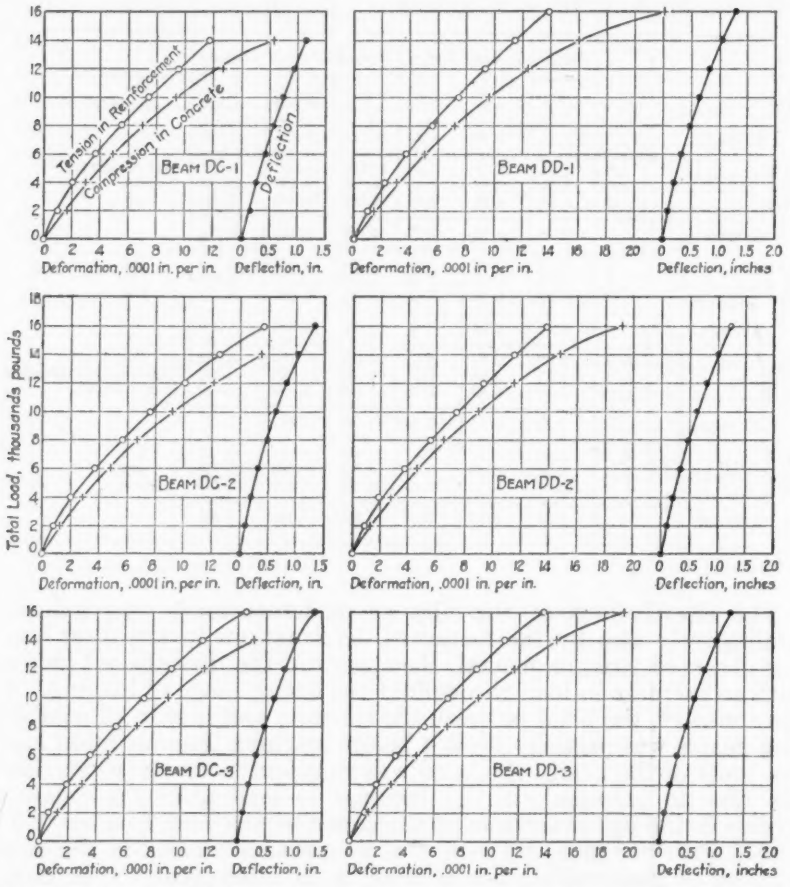

FIGURE 17.—*Load-deformation curves and load-deflection curves for beams DC and DD*

The elongations in the lower surface of the reinforcement are shown by open circles, the compressions in the upper surface of the concrete by crosses, and the deflections of the beams by filled circles.

that this is not the case, since it is shown in Section VIII that the procedures followed in construction and curing were, of those tried, the most unfavorable for developing a strong bond.

As previously noted, the tiles for the beams were thoroughly wetted, once about one-half hour before and again immediately preceding the placing of the concrete. This procedure was followed in order to prevent the absorption by the tiles of an appreciable amount of the mixing water of the concrete, which would have tended to produce a

stronger concrete in the combination beams than that in the concrete beams. By a careful proportioning of the concrete materials and by saturating the tiles and the forms it was hoped that the concrete in the beams would be of uniform strength. Damp storage was provided

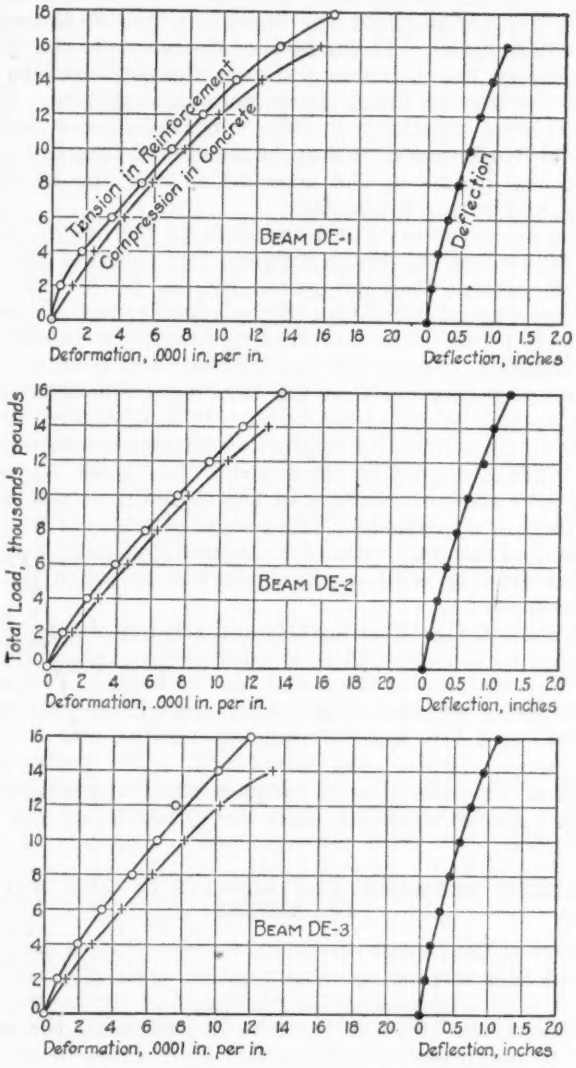

FIGURE 18.—*Load-deformation curves and load-deflection curves for beams DE*

The elongations in the lower surface of the reinforcement are shown by open circles, the compressions in the upper surface of the concrete by crosses, and the deflections of the beams by filled circles.

for the same reason; that is, to maintain more uniform curing conditions for the concrete than would have existed if beams of different sizes and forms had been permitted to dry out soon after construction. While this procedure probably was an aid in obtaining concrete of

uniform strength, it appears that it prevented the development of as strong a bond as would normally be obtained. It is shown in Section VIII that the strongest bond between concrete and hollow tile is obtained with tiles that are either dry or only moderately dampened at the time the concrete is placed. It is shown further that damp curing did not improve the bond as much as the compressive strength of the concrete. In the tests of the beams of the 1924 series [10] the bond between the concrete and tiles was sufficient to resist the tendency of the tiles to break away from the concrete. Since these earlier beams were constructed under conditions more nearly similar to commercial construction, it may be concluded that the weakness of the bond in the beams of the later series was due to the unusual construction and curing methods.

In Table 6 are given certain dimensions of the beams, the loads at which the failures of the bond between the concrete and tiles were noted, the maximum load supported by the beams and calculated quantities [11] giving an indication of the effectiveness of the tiles.

The computed maximum compressive stresses in the concrete were, with one exception, greater for the combination beams than for the concrete beams, indicating that the tiles were somewhat effective in spite of the partial failure of the bond. It is, of course, realized that the computed values for the compressive stresses corresponding to the maximum loads are greater than would be found by calculations which took into account changes in the modulus of elasticity of concrete with increases in stress. The results given, however, are based upon an assumed constant value for the modulus, since they may then be compared directly with working stresses to judge the factors of safety of designs.

The higher strengths of beams DD and DE over beams DB and DC are believed to be due entirely to the difference in the surface finish of the tiles. The surfaces of the 6-cell tiles in beams DB and DC were smooth except for rounded scores, while the surfaces of the 4-cell tiles in beams DD and DE were of rougher texture, and the grooves in these tiles were angular and dovetailed. The better mechanical bond obtained with the tiles of rough surface is probably the cause of the higher strengths rather than the difference in the number of cells in the tiles.

3. COMPARISONS BETWEEN THE RESULTS OF THE 1924 AND THE 1926 SERIES

In the tests of the beams of the 1924 series [12] the bond between the concrete and tiles seemed to remain intact until after the failures of the beams, the tiles increasing the resistance of the beams to bending. For these beams the effect of the tiles in increasing the resistance of the beams to compressive failures was equivalent to an increase in

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[10] Reported in B. S. Tech. Paper No. 291.

[11] Following the notation and formulas for rectangular beams given in the 1924 report of the Joint Committee on Standard Specifications for Concrete and Reinforced Concrete (see footnote 6):

The values of the computed maximum compressive stress (f_c) were derived from the formula $f_c = \frac{2M}{kjbd^2}$ in which the bending moment (M) for a beam was equal to that at mid span due to the maximum load, and the values of b and d were, respectively, the measured total width of the concrete ribs and depth of the steel. The values of k and j were computed on the basis of $n = 12$ by means of the formulas for rectangular beams of the joint committee, the only exception from the recommended procedure being that for the combination beams the ratio of reinforcement was taken as the area of reinforcement divided by the combined areas of the concrete ribs and the vertical tile shells.

[12] Reported in B. S. Tech. Paper No. 291.

the width of each concrete rib of from 2.0 to 4.5 inches, the amount for any one type of tile being approximately proportional to the product of the modulus of elasticity and the thickness of the tile shells.

The effect of the tiles on the stiffness of the beams was marked in both series. A comparison of the average of the deflections of the combination beams with similar values for the concrete beams is shown in Figure 19. For these beams (1926 series) the deflections of

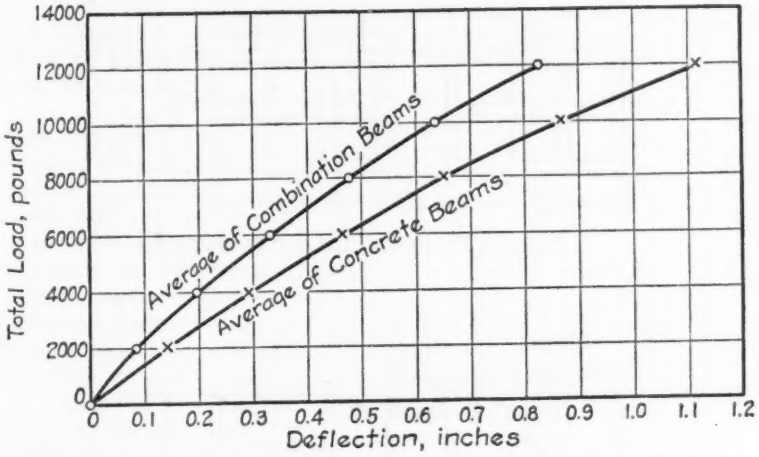

FIGURE 19.—*Average load-deflection curves for the concrete and for the combination beams*

the combination beams were, on the average, about 0.7 as great as for the concrete beams.

VIII. TESTS OF THE BOND BETWEEN CONCRETE AND HOLLOW TILE

The tests described in this section were made chiefly to obtain data which would be of assistance in interpreting the results of the tests of the series D beams. In particular, they were planned to obtain information on the effects of the following factors on the strength of the bond between concrete and hollow tile: (1) The absorption of the tiles, (2) the moisture content of the tiles at the time of placing the concrete, and (3) the proportions, consistency, and curing conditions of the concrete.

1. THE TEST SPECIMENS

(a) TYPE

As shown in Figure 20, the specimens for the bond tests resembled portions, 12 inches long and 28 inches wide, from a hollow tile and concrete slab 8 inches in depth. Each consisted of a concrete block (right prism) between two 8 by 12 by 12 inch tiles. The concrete blocks filled the 4-inch spaces between the tiles to the full depth of 8 inches. In the other direction only the central 9 inches along their length was filled. Thus 4 by 8 by 9 inch concrete blocks were formed, which were in contact over an 8 by 9 inch surface of each tile.

Although the method of producing bond stresses and the distribution of these stresses in specimens of this type differ materially from those in a slab, there are important features which are similar. In a slab the compressive strains in the concrete ribs tend to produce, through shearing bond stresses parallel to the cells of the tiles, corresponding strains in the tiles. The stresses in these test specimens which tend to break the bond are similar in nature and direction, even though their distribution is different than in a slab. Since the purpose of the tests was to compare the strengths of specimens of

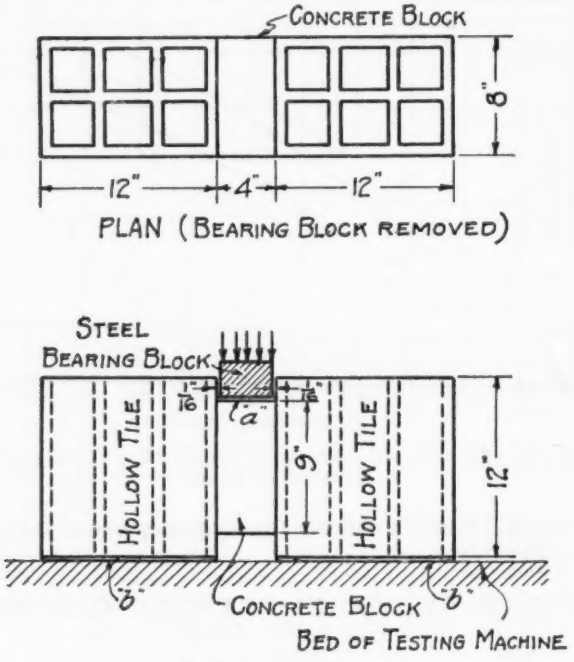

FIGURE 20.—*Details of specimens for the bond tests*

the same size and shape, but differing in materials and treatment, the absolute values obtained are not of great importance in this study.

(b) MATERIALS, CONSTRUCTION, AND AGING

The Kentucky shale tiles were of the same type and from the same plant as those of lot No. 4 used in the 1924 series of slab tests.[13] The tiles of Ohio fire clay were similar in the same way both to those of lot No. 3 of the 1924 series[13] and lot No. 1 (Table 4) of the present series, while the 6-cell and the 4-cell New Jersey fire-clay tiles were, respectively, from lots 3 and 5 (Table 4) of the present series.

The materials for the concrete were similar to those for the beams, and, except for differences in the proportions, were mixed and placed in the same manner. The mixtures listed in Table 7 were proportioned by dry rodded volumes, the proportion of sand to gravel being the same for all bond specimens.

[13] B. S. Tech. Paper No. 291, Table 3, p. 477.

TABLE 7.—*Results of the bond tests*

Reference No.	Kind of tile	Concrete: Mix	Concrete: Slump	Concrete: Water cement ratio (w/c) by volume	Moisture in tile before placing concrete	Water per cubic foot of wet concrete	Storage	Compressive strength 6 by 12 inch cylinder	Compressive strength of block	Ratio of block strength to cylinder strength	Bond strengths: Maximum	Bond strengths: Minimum	Bond strengths: Average of 5 tests
			Inches		*Per cent*	*Pounds*		*Lbs./in.²*	*Lbs./in.²*		*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*
1	Kentucky shale	1:2:4	8	1.25	0	14.08	Dry	1,400	1,010	0.72	225	125	186
2	do	1:2:4	8	1.25	[1] 3.3	14.08	do	1,400	830	.59	270	130	177
3	Ohio fire clay	1:2:4	8	1.25	0	14.08	do	1,400	1,410	1.00	374	222	277
4	do	1:2:4	8	1.25	[1] 5.4	14.08	do	1,400	840	.60	174	83	126
5	New York surface clay	1:2:4	8	1.25	0	14.08	do	1.400	1,200	.86	318	151	256
6	do	1:2:4	8	1.25	[2] 3.7	14.08	do	1,400	1,050	.75	300	185	238
7	do	1:2:4	8	1.25	[1] 21.4	14.08	do	1,400	720	.52	183	98	138
8	New Jersey 6-cell fire clay	1:2:4	8	1.25	0	14.08	do	1,400	1,570	1.12	382	200	295
9	do	1:2:4	8	1.25	[2] 1.4	14.08	do	1,400	1,560	1.11	409	180	286
10	do	1:2:4	8	1.25	[2] 1.3	14.08	Damp	1,400	1,490	1.06	395	104	235
11	do	1:2:4	6	1.15	[2] 1.2	13.07	Dry	1,550	1,610	1.04	500	214	373
12	do	1:2:4	9	1.35	[2] 1.0	15.10	do	1,060	1,320	1.25	366	160	301
13	do	1:1.5:3	8	.98	[2] 1.5	14.22	do	2,200	1,920	.87	441	306	354
14	do	1:1.5:3	8	.98	[2] 1.6	14.22	Damp	2,200	2,110	.96	381	137	274
15	do	1:2:4	8	1.25	[2] 9.6	14.08	Dry	1,400	950	.68	278	136	190
16	New Jersey 4-cell fire clay	1:2:4	1¾	1.00	0	11.51	do	1,910	1,960	1.03	385	279	324
17	do	1:1.5:3	8¼	1.00	0	14.48	do	1,930	1,530	.79	265	177	242
18	do	1:2.5:5	3	1.25	0	11.80	do	1,400	1,760	1.26	395	255	312
19	do	1:2:4	8	1.25	0	14.08	do	1,150	1,370	1.19	284	210	245
20	do	1:2:4	1¾	1.00	0	11.51	Damp	1,910	2,000	1.05	354	247	278
21	do	1:2:4	8	1.25	0	14.08	do	1,150	1,540	1.34	333	248	288
22	do	1:1.5:3	8	1.08	[1] 9.6	14.48	do	2,050	1,600	.78	203	163	171
23	Kentucky shale	1:1.5:3	6¼	.93	0	13.57	Dry	2,300	1,760	.77	333	209	283
24	do	1:1.5:3	6¼	.93	0	13.57	Damp	2,300	2,000	.87	405	287	371

[1] Tiles immersed in water at 70° F. for 24 hours before concreting.

[2] Tiles dipped in water at 70° F. for 5 seconds before concreting.

The tiles for the bond specimens were first dried to constant weight; then, before making the bond specimens, some were dampened by dipping in water for 5 seconds, others were completely immersed in water for 24 hours, and the remainder were used without wetting. The bond specimens were made with the cells of the tiles in a horizontal position. The concrete was mixed by hand, one bond specimen and one 6 by 12 inch cylinder being made from each batch.

From 24 to 48 hours after the specimens were made they were removed from the molds and placed in storage. The 6 by 12 inch concrete cylinders were kept in damp storage until ready for testing. Some of the bond specimens were kept in damp storage until 14 days old and then were allowed to dry 14 days before testing; the others were kept in dry storage. All specimens were tested when 28 days old.

2. TESTING

Previous to testing, the bond specimens were capped, as indicated in Figure 20, with a 2:1 cement-gypsum paste on the upper surface of the concrete block (marked "*a*") and on the bearing surface of the tiles (marked "*b*"). In testing the bond specimens the tiles were supported on the base of the testing machine, and the load was applied through a spherical bearing and a machined steel block to the upper surface of the concrete block. After the concrete blocks had been broken from the tiles in the bond tests they were capped with plaster of Paris on their 4 by 8 inch surfaces and tested in compression.

For the specimens made with saturated tiles, the concrete blocks remained intact and broke away from the tiles at the contact surfaces. In the other specimens the failures were accompanied by shearing in the concrete adjacent to the tile surfaces. In a few cases the blocks were broken to such an extent that they were not suitable for compressive tests, these failures usually being caused by diagonal cracks which started at the top and extended downward at an angle of about 45° from one tile to the other. The friction between the specimen and the base of the testing machine seemed to be great enough to prevent the tiles from breaking away from the bedding during a test. The movement and deformation of the tiles were measured during the test of one bond specimen. It was found that there was compression in the entire cross sections of the tiles and that the tiles separated more at the top than at the bottom.

3. RESULTS OF THE TESTS

The details regarding the materials for the specimens and the results of the tests are given in Table 7. The New Jersey fire-clay tiles used in the bond tests were samples selected from two of the lots for the beams, the 6-cell and the 4-cell being, respectively, lots 3 and 5.

(a) EFFECT OF THE STRENGTH OF THE CONCRETE ON THE STRENGTH OF THE BOND

Figure 21 shows graphically a comparison between the compressive strength of the concrete blocks and the bond strengths. The results from the dry-cured specimens are shown by filled characters and the values for the damp-cured specimens are shown by open characters. The line shown is the graph of a linear equation which best represents the trend of the values for the dry-cured specimens, without regard

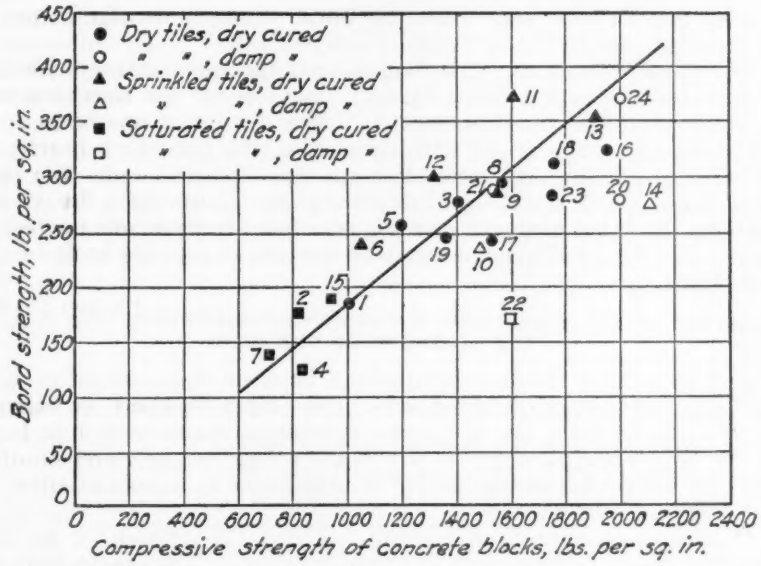
Dry tiles, dry cured
" " , damp "
Sprinkled tiles, dry cured
" " , damp "
Saturated tiles, dry cured
" " , damp "
Bond strength, lb. per sq. in.
Compressive strength of concrete blocks, lbs. per sq. in.
0 50 100 150 200 250 300 350 400 450
0 200 400 600 800 1000 1200 1400 1600 1800 2000 2200 2400

FIGURE 21.—*Relation between the bond and the compressive strength of the concrete blocks*

The numbers refer to the reference numbers given in Tables 7 and 8. The line is intended to represent the trend of values for the dry-cured specimens only.

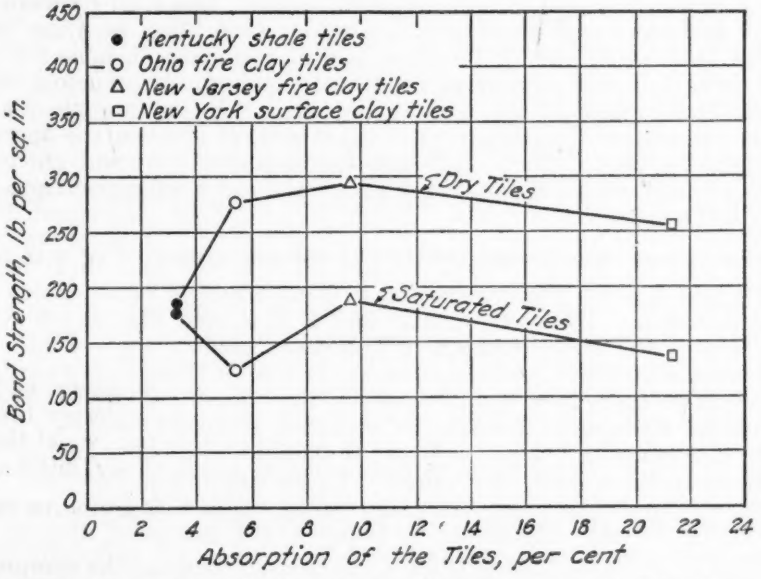
Kentucky shale tiles
Ohio fire clay tiles
New Jersey fire clay tiles
New York surface clay tiles
Dry Tiles
Saturated Tiles
Bond Strength, lb. per sq. in.
Absorption of the Tiles, per cent
0 50 100 150 200 250 300 350 400 450
0 2 4 6 8 10 12 14 16 18 20 22 24

FIGURE 22.—*Effect of the absorption and the moisture content of the tiles on the bond*

The comparisons shown are confined to values from the dry-cured specimens made with 1:2:4 concrete.

for the others. Although there is a considerable scattering of the plotted points, it is seen that the bond strength usually increased with an increase in the strength of the concrete.

The bond strengths of the damp-cured specimens made with tiles of medium absorption (New Jersey) were less for the same concrete strength than the bond strengths of the dry-cured specimens. Of the damp-cured specimens with these tiles, the lowest bond strength for a corresponding concrete strength was obtained with the saturated tiles. With the tiles of low absorption (Kentucky), the relation between the bond strength and the concrete strength was not appreciably affected by either the moisture content of the tiles or the curing conditions.

(b) EFFECT OF THE ABSORPTION AND MOISTURE CONTENT OF THE TILES ON THE STRENGTH OF THE BOND

In Figure 22 is shown a comparison between the absorption of the tiles and the strength of the bond. The values for the bond strength were obtained from the dry-cured specimens made with 1:2:4 concrete. The absorption of the tiles is the weight of the water absorbed after 24 hours' immersion at 70° F. expressed as a percentage of the dry weight of the tiles.

With specimens built with saturated tiles, the strength of the bond was practically independent of the absorption. The specimens made from dry tiles having absorptions from 5 to 20 per cent did not show a wide variation in bond strength. Except with the tiles of lowest absorption, there was a material decrease in bond strength due to the tiles being saturated at the time the concrete was placed. Practically no difference in bond strength existed, however, between the dry and saturated shale tiles having an absorption of 3 per cent. The bond strengths of the three sets of specimens 5, 6, and 7 and likewise 8, 9, and 15 may be compared to determine the effect of the moisture content of the tiles at the time the concrete was placed, those in each of the two groups of three being of identical construction except for this factor. Although the strengths were markedly less with saturated tiles, they were about the same with the dipped as with the dry tiles.

(c) EFFECT OF THE CURING CONDITIONS ON THE STRENGTH OF THE BOND

Table 8 shows the comparison in bond strength between dry and damp curing. From Groups D and F it is seen that damp curing increased the bond strength of specimens made from dry tiles and comparatively wet concrete, whereas in Group E the damp curing of specimens made from a comparatively dry concrete showed a decrease in bond strength. It might be expected, therefore, that the damp-cured specimens in Groups A and B should also develop higher bond strength than those dry cured. These specimens, however, were made from dipped tiles, and damp curing resulted in lower strengths than dry curing. As shown by Group C still less bond strength was obtained with saturated tiles. The indications are that with damp curing the bond strength is less the greater the moisture content in the tile.

TABLE 8.—*Results of bond tests showing the effect of the curing conditions on the bond*

Reference No.	Group	Kind of tile	Mix	Slump	Storage	Treatment of tiles before placing concrete	Bond strength
				Inches			*Lb./in.²*
9	A	New Jersey fire clay, 6 cell	1:2:4	8	Dry	Dipped	286
10	A	do	1:2:4	8	Damp	do	235
13	B	do	1:1½:3	8	Dry	do	354
14	B	do	1:1½:3	8	Damp	do	274
22	C	New Jersey fire clay, 4 cell	1:1½:3	8	do	Saturated	177
19	D	do	1:2:4	8	Dry	Dry	245
21	D	do	1:2:4	8	Damp	do	288
16	E	do	1:2:4	1¾	Dry	do	324
20	E	do	1:2:4	1¾	Damp	do	278
23	F	Kentucky shale	1:1½:3	6¼	Dry	do	283
24	F	do	1:1½:3	6¼	Damp	do	371

(d) EFFECT OF THE PROPORTIONS OF THE CONSTITUENTS OF THE CONCRETE ON THE STRENGTHS OF THE CONCRETE CYLINDERS AND BLOCKS

It was shown by Figure 21 that, in general, the strength of the bond increased with an increase in the strength of the concrete blocks between the tiles. The strength of the concrete cylinders, made and cured by the methods commonly employed for control specimens of this type, may be taken as measures of the quality of the concrete mixtures used in the bond specimens. Since, however, there was neither a close relation between the strengths of the cylinders and the blocks made from the same mixes nor between the strengths of the cylinders and the bond strengths, it would be of value to determine, if possible, the factors which caused the large variations in the relation between the strengths of the cylinders and the blocks. For the present purposes it is not necessary to include in this study the effects of such factors as the form of test specimen and curing conditions, since we are not concerned because the strengths are different, but only because the strengths of the two different specimens are not related.

It has been shown that the strengths of concrete cylinders made from the same cement, and with the same type and grading of aggregates, and by the same process are closely related to the ratios of the volumes of water and cement (water-cement ratio) in the mixes.[14] With concrete cast in nonabsorptive forms the water-cement ratio of the mix may be calculated readily when the amount of each ingredient and the absorption of the aggregate are known. When, however, concrete is molded in porous forms, such as hollow tiles, some of the mixing water is absorbed and the effective water-cement ratio is less than the values so calculated. With concretes having such workable properties that they may be compacted in the forms, a reduction in the water-cement ratio may be expected to cause an increase in the strength of the resulting concrete. It would be expected, further, that the effect of the absorption of the tiles on the water-cement ratios, and consequently on the strength of the concrete blocks, would be most pronounced with the mixes containing the least amount of water, since with a given absorption the less the amount of water present in the mix the greater the percentage reduction.

[14] Abrams, Bulletin No. 1, Lewis Institute, Chicago, Ill.

In Figure 23 values from the dry-cured specimens made with dry and dipped New Jersey fire-clay tiles are shown graphically to illustrate the effect of the amount of water in the batches on the ratios between the strengths of the cylinders and the block. The values for the water-cement ratio of the concrete as mixed are shown adjacent to the plotted points. Dashed lines sloping upward to the left were drawn empirically to represent contours of equal water-cement ratios. The leaner mixes are at the upper portions of the curves. It is seen from Figure 23 that the ratio of block strength to cylinder strength increased as the water-cement ratio increased and as the amount of water in the batch decreased. The ratio of block strength was greatest,

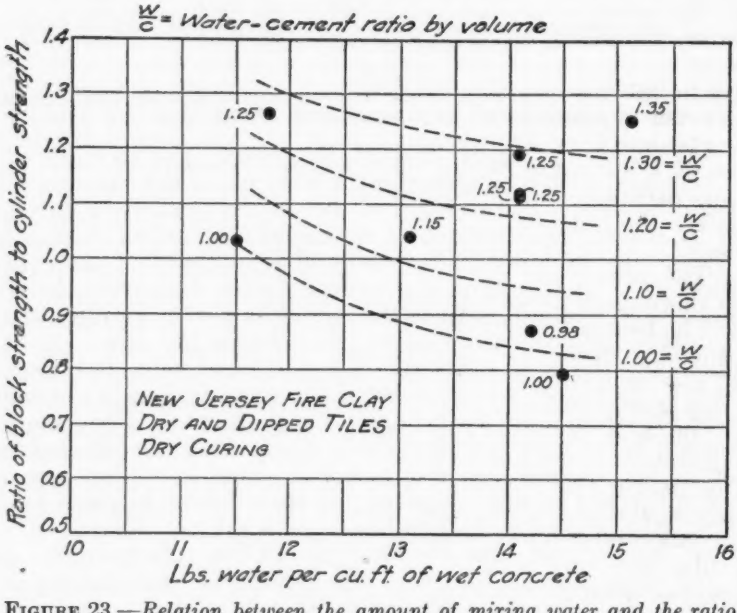

FIGURE 23.—*Relation between the amount of mixing water and the ratio of block strength to cylinder strength*

therefore, with lean concrete mixtures of comparatively dry consistency. These conclusions obviously would be different with specimens consisting of a thin bed of mortar or concrete in contact with absorptive forms.

4. CONCLUSIONS

In general, the results of these tests indicate that the strength in shear of the bond between hollow tiles and concrete was greatest when concrete containing the minimum amount of water necessary for its proper placement was used in combination with dry or dipped tiles of medium absorption. Some of the concrete mixtures used in the test specimens probably were of drier consistency than could be placed properly in commercial construction, and for this reason the apparent advantage of the driest mixtures might not be realized in practice.

In particular it may be stated that—

1. For dry-cured specimens the bond strength in shear increased with the strength of the concrete blocks between the tiles.
2. For specimens made from dry tiles the bond strength in shear did not vary widely with tiles having absorptions between 5 and 20 per cent.
3. With tiles having absorptions between 5 and 20 per cent, the bond strength in shear was markedly less for specimens made with saturated tiles than with those made with dry or dipped tiles.
4. Except with specimens made with dry tiles and concrete of wet consistency (slumps 6¼ and 8 inches), the bond strengths in shear were greater for the dry-cured than for the damp-cured specimens.
5. For specimens made from New Jersey fire-clay tiles the ratio between the strengths of the concrete blocks and the cylinders increased as the water-cement ratio increased and as the amount of water in batch decreased.

In order to judge whether the methods followed in the construction of the beams of series D were favorable or unfavorable to the development of a strong bond between the concrete and hollow tile, the factors pertaining to the beams, which were found in the bond tests to affect the bond, may be recalled. They may be summarized as follows:

1. The tiles were of medium absorption (New Jersey clay) and were thoroughly wetted before the concrete was placed.
2. The beams were kept in damp storage for 28 days and were then kept in dry storage for 2 weeks before testing.
3. The concrete for the beams was of wet consistency. The average slump of the concrete was 9.4 inches; the water-cement ratio was 1.00; and the mixes contained 18 pounds of water per cubic foot of concrete.

Comparing these factors with the results of the bond tests, it is seen that the wetting of the tiles and the damp curing of the beams were unfavorable to the development of strong bond. Since, however, the tiles were wet when the concrete was placed, the effect of the amount of mixing water in the concrete on the absorption of the water by the tiles was not important.

WASHINGTON, August 28, 1929.

ENDURANCE PROPERTIES OF SOME SPECIAL RAIL STEELS

By John R. Freeman, Jr., and R. D. France

ABSTRACT

A series of tests have been carried out to determine the endurance properties of steel from heat-treated rail: Medium manganese rail, a zirconium-treated medium manganese rail, and a manganese molybdenum rail. Results are also given of some tests made on steel from a transverse fissured rail and an unfissured rail from the same heat that had been subjected to similar traffic. Heat treatment of rails was found to have markedly increased the endurance limit of the steel. Medium manganese rail steels were found, in general, to have a higher endurance limit than carbon rail steels. The manganese molybdenum rail steel had approximately the same endurance limit as the medium manganese rail. The steel in the fissured rail was found to have approximately the same endurance limit as steel from the unfissured rail.

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I. INTRODUCTION

The Bureau of Standards was requested by the special joint subcommittee of the Rail Manufacturers Technical Committee and the Rail Committee of the American Railway Engineering Association to determine the endurance properties of some special heat-treated rail steels and of the so-called "medium manganese rail" steels. The bureau was also requested by G. N. Eaton, of the Molybdenum Corporation of America, to determine the endurance properties of a special manganese molybdenum rail and by Dr. G. B. Waterhouse to make similar tests on a zirconium-treated medium manganese rail.

The proposed tests fitted in with the general program of study of the endurance properties of rail steels then in progress [1, 2] as a part of

[1] Freeman, John R., jr., Dowdell, R. L., and Berry, W. J., Endurance and Other Properties of Rail Steel, B. S. Tech. Paper No. 363. Throughout this report the above papers are referred to as the "previous reports."

[2] Freeman, John R., jr., and Solakian, H. N., Effect of Service on Endurance Properties of Rail Steels, B. S. Jour. Research, 3 (RP 92); August, 1929.

the broader investigation seeking to determine the cause of transverse fissure failure in rails.

Tests have therefore been made on these materials using the same equipment and under the same conditions as in the tests previously reported. All tests were on specimens from new rail.

II. MATERIAL STUDIED

1. MEDIUM MANGANESE RAIL

In recent years some of the railroads in the United States have been using in increasing amounts a rail steel containing approximately 1.2 to 1.7 per cent manganese and 0.50 to 0.70 per cent carbon.[3] Rail of this approximate composition has been termed "medium manganese rail" to distinguish it from the well-known 12 to 14 per cent manganese steel rail that has been extensively used in switches, crossovers, and similar locations subject to great wear.

The medium manganese rails used in the tests reported here were made by the Bethlehem Steel Co., at Steelton, Pa., for the Delaware, Lackawanna & Western Railroad. The chemical compositions are given in Table 1 (M–1, M–2). Tests were made on A, D, and F rails, representative of two heats with slightly different manganese and carbon contents.

TABLE 1.—*Composition of rail steels studied*

Type of steel rail	Bureau of Standards designation heat No.	Manufacturers heat No.	C	Mn	P	S	Si	Mo	Zr
			Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Medium manganese [a]	M–1	88227	0.655	1.53	0.030	0.057	0.29	----	----
	M–2	89235	.590	1.21	.022	.045	.21	----	----
Heat treated (30 seconds quench).[b]	H–1–A	86124–A–9	.73	.60	.026	.050	.25	----	----
	H–1–C	86124–C–3							
	H–1–F	86124–F–1							
Heat-treated (15 seconds quench).[c]	H–2–A	88074–A–7	.74	.63	.024	.070	.31	----	----
	H–2–C	88074–C–8							
	H–2–F	88074–F–10							
Comparison rail [d]	H–3–C	87173–C–11	.82	.67	.023	.040	.34	----	----
	H–3–F	87173–F–2							
Manganese molybdenum.[e]	E–1	----	.45	1.70	.024	.010	.16	0.38	----
Zirconium treated medium manganese.[f]	K–1	84–J–254	.63	1.56	.024	.033	.32	----	----
			[g].65	[g]1.59	[g].014	[g].032	[g].32	----	[g]0.09

[a] Ladle analysis, medium manganese rail steel, Bethlehem Steel Co. R. E. 130-pound section. For Delaware, Lackawanna & Western R. R.

[b] Ladle analysis, Bethlehem Steel Co. rails quenched 30 seconds in water. Heated after quenching at 950° F. for 1½ hours, then air cooled. P. S. 130-pound section. For Pennsylvania R. R.

[c] Ladle analysis, Bethlehem Steel Co. Rails quenched 15 seconds in water. Heated after quenching at 950° F. for 1½ hours, then air cooled. P. S. 130-pound section. For Pennsylvania R. R.

[d] Ladle analysis, Bethlehem Steel Co. Carbon rail steel, normal practice P. S. 130-pound section. For Pennsylvania R. R.

[e] From O position, Mn–Mo rail from Molybdenum Corporation of America.

[f] Ladle analysis, zirconium-treated medium manganese rail steel, Bethlehem Steel Co. For Boston & Maine R. R.

[g] From O position.

[3] Report of Committee on Rail, Bulletin, Am. Ry. Eng. Assoc., **30**, No. 315, Appendix G, March, 1929.

2. HEAT-TREATED RAILS

The heat-treated rails were made in accordance with the Kenny process.[4] The rails used for the tests reported here were, after rolling, allowed to cool until the base became slightly magnetic as determined by a magnet. The rails were then quenched in water for a predetermined number of seconds. They were then immediately transferred into a furnace preheated to 950° F., held at that temperature for one and one-half hours, then drawn out and allowed to cool in air.[5] The chemical compositions and time of quenching are also given in Table 1. (H–1 and H–2.)

For comparison with the heat-treated rails tests were also made on rails from a normal heat designated as H–3, details of which are also given in Table 1.

3. MANGANESE MOLYBDENUM RAIL

In the search for a superior rail manganese molybdenum steel has been proposed by the Molybdenum Corporation of America and service test rails are now in track.

Unfortunately details of manufacture of the rail on which tests are reported here are not available. It was an A rail and had the composition as determined by analysis from the O position, as given in Table 1.

4. ZIRCONIUM-TREATED MEDIUM MANGANESE RAIL

This rail was from a special heat of rail steel made at the Bethlehem Steel Co. for the Boston & Maine Railroad. The sample was an F rail taken from the seventh ingot of heat No. 84J254. The ingots were of 7-rail length so that the sample came from the top of the next to the last rail of the ingot. The steel was poured in the usual way into ordinary molds 25 by 30 inches at the butt, and the ingots were poured 83 inches long. The composition is given in Table 1.

III. TEST METHODS

There was some question whether the hardness of the heat-treated rails would be uniform across the section because of the well-known mass effect in quenching. It is well known that an approximate relation exists between the hardness and endurance properties of steel. Therefore, if a marked difference in hardness were present it is obvious that fatigue tests made on specimens taken across the section, as in previously reported tests, would be expected to show considerable scatter due to the difference in properties between the central and outer portions of the head of the rail.

A hardness survey was, therefore, made of all of the rails. Both Rockwell B and Brinell numbers were determined at the points indicated in Figure 1. As will be noted later no appreciable difference in hardness between center and outer portions of the heads of the heat-treated rails was apparent. The endurance test specimens were, therefore, taken from all rails in the same manner as described fully in the previous reports.

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[4] Kenny, E. F., U. S. Patent No. 1619025, Mar. 1, 1927; and reissue No. 17240 Mar. 19, 1929.
[5] Private communication from H. B. Bent, engineer of tests, Bethlehem Steel Co., Steelton, Pa.

For convenience, the figure showing location of test specimens is repeated here. (Fig. 2.) Duplicate contiguous (end to end) specimens were taken giving a group of 12 specimens from each rail. They were taken from adjoining portions to those on which the hardness tests were made. All test sections were taken from a location at least 1 foot from the end of the rail.

All tests were made in a rotating beam type (R. R. Moore design) of endurance testing machine. At least one of each group of test specimens was subjected to 25,000,000 cycles of stress at a value just under the endurance limit. All other specimens were run at least

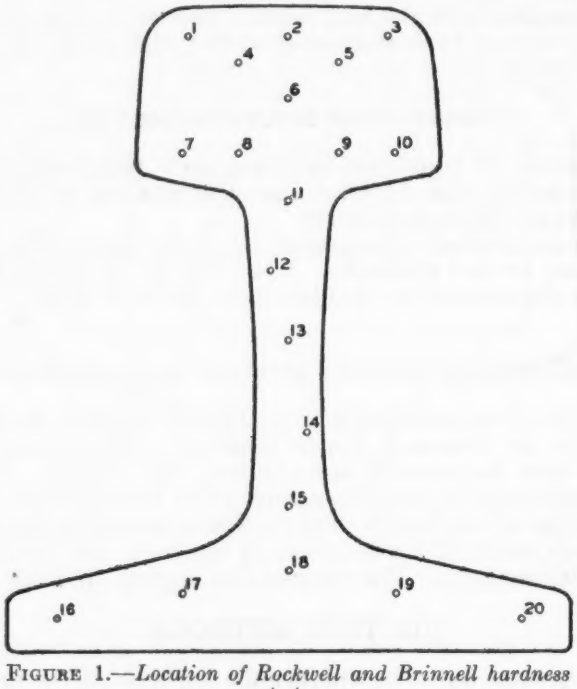

FIGURE 1.—*Location of Rockwell and Brinnell hardness tests*

10,000,000 cycles if failure did not occur previously. In all cases a specimen that was run 25,000,000 cycles was restressed at a value considerably above the endurance limit to determine whether understressing had occurred.

Tensile tests were made using standard 0.505-inch diameter test bars having 2-inch gage length taken from the O position, of rails representative of all heats.

IV. RESULTS OF TESTS

1. HARDNESS SURVEY

The results of all hardness tests have been incorporated in Table 2 (*a*) and (*b*). Examination of the data shows quite definitely that there is no measurable difference in hardness between the center and outer portions of the heat-treated or other rail sections.

The maximum hardness is shown by the rails of heat H–1 which were quenched for 30 seconds. The hardness of the rails of heat H–2 which were quenched for only 15 seconds is, in general, intermediate between the untreated "normal practice" rails of heat H–3 and the rails quenched for 30 seconds (heat H–1).

There is very slight, if any, significant difference in the hardness of the medium manganese, manganese-molybdenum, zirconium-treated and normal practice carbon steel rails.

2. TENSILE TESTS

The results of tensile tests are given in Table 3. As was indicated by the hardness tests the steel from rails quenched for 30 seconds

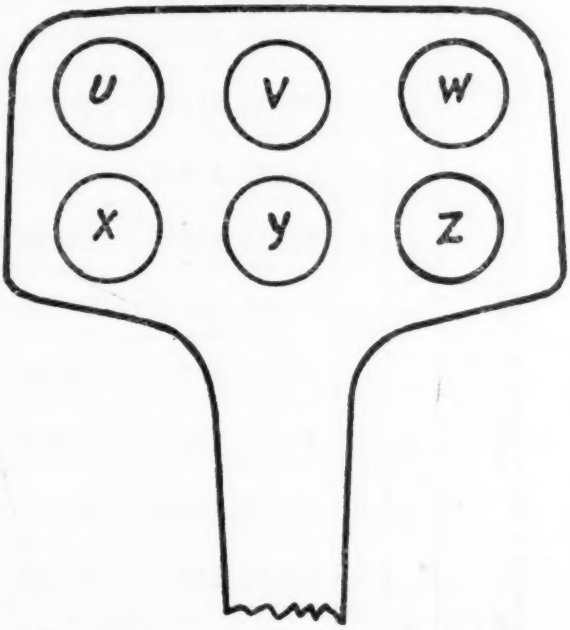

FIGURE 2.—*Location of endurance test specimens*

(H–1) showed the highest tensile strength. The steel from the rails quenched for 15 seconds (H–2) had appreciably lower values, but greater strength than the "normal practice" rail steel. The tensile strength of the medium manganese rail steel (M–1) containing 1.5 per cent manganese is apparently somewhat higher than that of the normal practice rail steel. On the other hand, the medium manganese rail steel containing 1.2 per cent manganese (M–2) has an indicated tensile strength appreciably lower than the normal practice rail steel and is approximately the same as that of the manganese-molybdenum rail steels. The magnitude of the difference in tensile strengths between the unheat-treated rail steels, however, is not great and might be accounted for by differences in rates of cooling particularly in the alloy steels. The total number of tests made are also too few to draw any definite conclusions.

TABLE 2

(a) ROCKWELL B HARDNESS SURVEY OF RAIL SECTIONS

Position in section (fig. 1)	Rockwell B hardness No.															
	Heat H–1 (30 seconds quench)			Heat H–2 (15 seconds quench)			Heat H–3 (normal practice)		Heat M–1 (1.5 per cent Mn)			Heat M–2 (1.2 per cent Mn)			Heat E–1 (1.7 per cent Mn, 0.38 per cent Mo)	Heat K–1 (1.56 per cent Mn, 0.63 per cent C. Zr treated)
	Rail			Rail			Rail		Rail			Rail			Rail	Rail
	A	C	F	A	C	F	C	F	A	D	F	A	D	F	A	F
1	109	108	106	105	100	101	103	102	103	95	101	99	102	102	102	106
2	110	110	109	106	100	102	102	102	101	98	100	99	100	101	103	103
3	110	109	107	105	105	106	103	102	103	99	99	102	101	102	103	104
4	109	110	109	107	102	105	103	103	102	99	91	100	101	102	104	103
5	111	111	111	108	103	103	102	103	103	101	96	99	101	102	103	105
6	111	110	109	105	101	106	102	101	104	98	104	101	101	100	104	102
7	109	110	108	107	103	104	104	102	106	100	90	102	103	102	104	105
8	112	111	109	107	102	104	102	102	100	95	88	103	102	101	103	103
9	110	111	110	107	108	103	103	102	104	94	101	101	101	102	103	103
10	111	111	111	108	105	106	104	103	106	100	101	101	102	102	105	104
Average hardness of railhead	110.2	110.1	108.9	106.5	102.9	104	102.8	102.2	102.9	97.4	97.1	100.7	101.4	101.6	103.4	103.8
11	114	111	110	108	103	105	104	103	107	103	100	104	102	100	108	105
12	111	112	111	108	105	105	103	104	105	97	95	103	102	100	104	104
13	112	112	109	107	104	105	103	101	107	101	101	100	102	100	103	104
14	110	112	109	106	104	103	100	101	106	99	95	99	103	101	104	103
15	112	111	110	109	104	104	100	102	106	104	102	101	102	101	105	106
16	111	112	111	109	107	109	105	103	106	95	94	101	103	103	104	105
17	111	111	110	108	103	106	101	104	103	94	98	102	102	102	104	106
18	111	111	110	108	104	106	101	101	103	96	97	101	101	101	104	104
19	111	111	110	109	105	107	102	102	105	102	99	100	100	102	103	106
20	112	112	111	109	107	110	102	104	107	102	101	102	101	102	103	104
Average hardness, web and base	111.5	111.6	110.0	108.1	104.6	106.0	102.1	102.5	105.5	99.3	98.2	101.3	101.6	101.2	104.2	104.7

(b) BRINELL HARDNESS (3,000 KG LOAD) SURVEY OF RAIL SECTIONS

Position in rail (figs. 1 and 2)	Brinell hardness No.															
	Heat H–1 (30 seconds quench)			Heat H–2 (15 seconds quench)			Heat H–3 (normal practice)		Heat M–1 (1.5 per cent Mn)			Heat M–2 (1.2 per cent Mn)			Heat E–1 (1.7 per cent Mn, 0.38 per cent Mo)	Heat K–1 (1.56 per cent Mn, 0.63 per cent C. Zr treated)
	Rail			Rail			Rail		Rail			Rail			Rail	Rail
	A	C	F	A	C	F	C	F	A	D	F	A	D	F	A	F
U	363	350	341	321	311	302	285	285	282	285	269	255	255	255	269	302
V	363	352	345	306	300	302	272	285	272	262	255	244	248	252	269	285
W	359	341	341	321	319	304	285	285	293	282	269	244	252	255	266	298
X	363	354	345	321	317	306	269	285	282	269	262	252	255	255	262	293
Y	415	354	325	304	277	285	285	285	302	266	277	255	248	241	272	269
Z	361	347	341	321	317	317	283	285	282	277	269	262	262	255	272	288
Average hardness of head	370.7	349.7	339.7	315.7	306.8	302.7	279.8	285.0	285.5	273.5	265.8	252.0	253.3	252.2	268.3	292.5
11	415	359	337	341	286	302	285	269	302	272	288	266	255	241	282	277
13	388	363	341	339	302	313	285	269	306	269	288	262	262	248	269	288
15	375	350	341	341	317	321	277	272	288	269	277	255	255	241	282	272
16	383	363	352	331	321	345	302	288	302	266	272	255	255	255	262	298
20	375	361	361	321	319	341	302	298	293	277	277	266	255	248	262	293
Average hardness of web and base	387.2	359.2	346.4	334.6	313.0	324.4	290.2	281.2	298.2	270.6	280.4	260.8	256.4	246.6	271.6	286.0

TABLE 3.—*Tensile and endurance properties of rail steels studied*

Heat No.	Rail	Tensile strength	Yield point	Elongation in 2 inches	Reduction of area	Endurance limit	Endurance ratio R
		Lbs./in.[2]	*Lbs./in.*[2]	*Per cent*	*Per cent*	*Lbs./in.*[2]	
H-1	A	175,500	----------	8.0	12.6	77,000	0.44
	C	167,000	----------	----------	----------	[1] 68,500	.41
	F	176,000	115,000	9.5	15.2	74,000	.42
Average A, C, F rails, heat H-1.		172,833	----------	----------	----------	73,166	.423
H-2	A	157,500	112,000	14.0	23.0	80,000	.51
	C	154,000	107,500	15.5	34.7	[1] 76,000	.49
	F	154,000	106,000	13.5	23.7	>67,000)	>.43)
Average A, C, F rails, heat H-2.		155,166	108,540	14.3	27.13	>74,000)	>.47)
H-3	C	139,000	91,500	11.0	15.2	59,500	.43
	F	140,000	80,000	11.0	15.2	55,500	.40
Average C and F rails, heat H-3.		139,500	85,720	11.0	15.2	57,500	.415
M-1	A	148,500	89,500	12.0	23.7	65,400	.44
	D	148,500	87,000	14.0	26.0	69,600	.47
	F	148,500	----------	13.5	25.1	67,000	.45
Average A, D, F rails, heat M-1.		148,500	----------	13.16	24.93	67,366	.453
M-2	A	129,500	75,000	16.0	28.8	52,800	.41
	D	135,000	----------	14.5	28.0	55,100	.41
	F	128,500	74,500	16.0	29.8	54,800	.43
Average A, D, F rails, heat M-2.		131,000	----------	15.5	28.87	54,233	.413
E-1	A	128,500	----------	18.0	44.0	62,600	.49
K-1	F	145,500	90,000	16.0	34.0	65,000	.45

[1] Specimens taken as indicated in Figure 2. A difference was found in endurance limits as indicated by specimens taken from the U and Y positions, respectively.

3. ENDURANCE PROPERTIES OF MEDIUM MANGANESE RAILS

The results of the endurance tests of the medium manganese rail steels are given in Figures 3 to 8, inclusive. The data for this series and all other series are presented in the customary form of S–N diagrams as was used in the previous reports. As in the previous studies the endurance curves plotted are those obtained on the duplicate bars taken from the U, V, W, X, and Z positions in the head of the rail. The results of tests on the Y specimens, determined later, are indicated in the plot by the letter Y, beside the respective plotted values.

The endurance ratio R (ratio of endurance limit to tensile strength) is also given in the respective plots.

The results of tests on the specimens from the A rail of heat M–1 (1.5 per cent Mn) are given in Figure 3. The data indicate an endurance limit of 65,400 lbs./in.^{2} for this steel. The "scatter" is relatively very slight, indicating that the steel is relatively homogeneous across the section of the head of the rail.

The results of tests of specimens from the D rail of the same heat are given in Figure 4. An endurance limit of 69,600 lbs./in.^{2} is indicated. The scatter of results is somewhat greater than was indicated for the A rail.

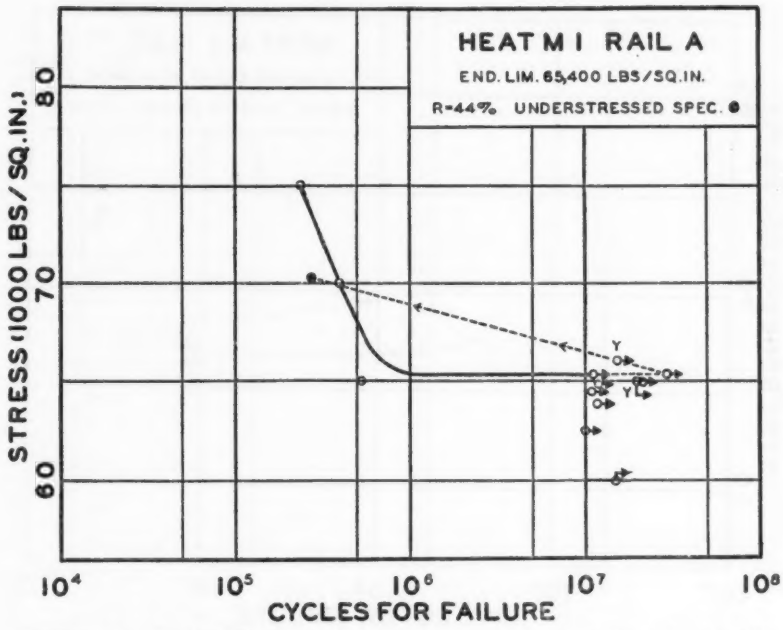

FIGURE 3.—*Endurance curve for medium manganese rail steel, A rail, heat M–1*

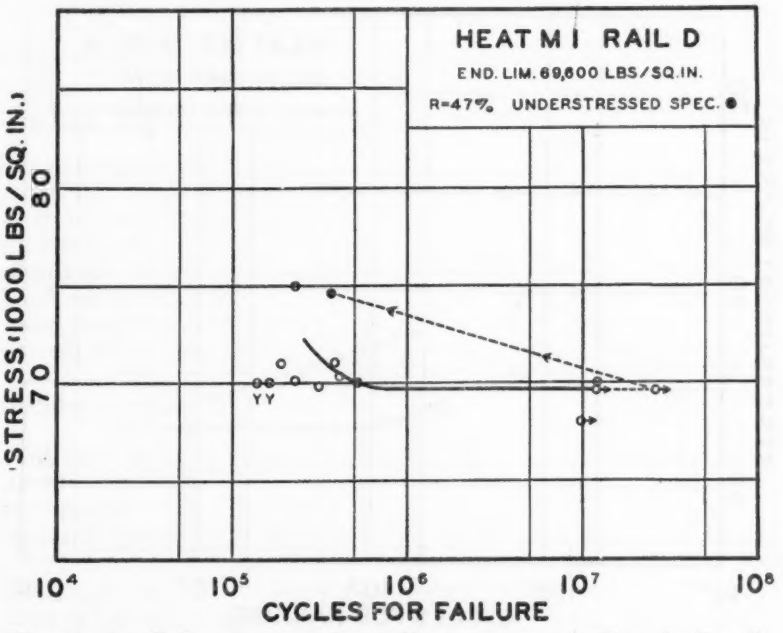

FIGURE 4.—*Endurance curve for medium manganese rail steel D rail, heat M–1*

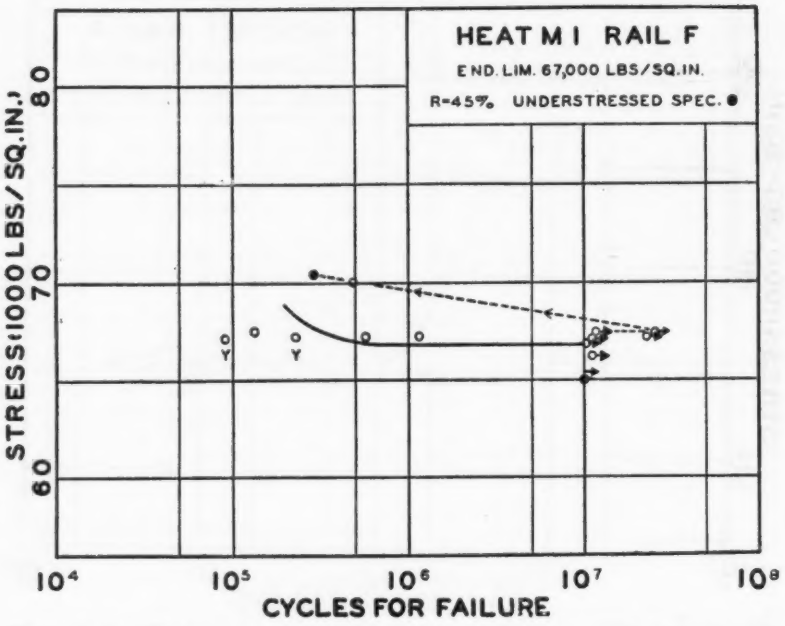

FIGURE 5.—*Endurance curve for medium manganese rail steel, F rail, heat M–1*

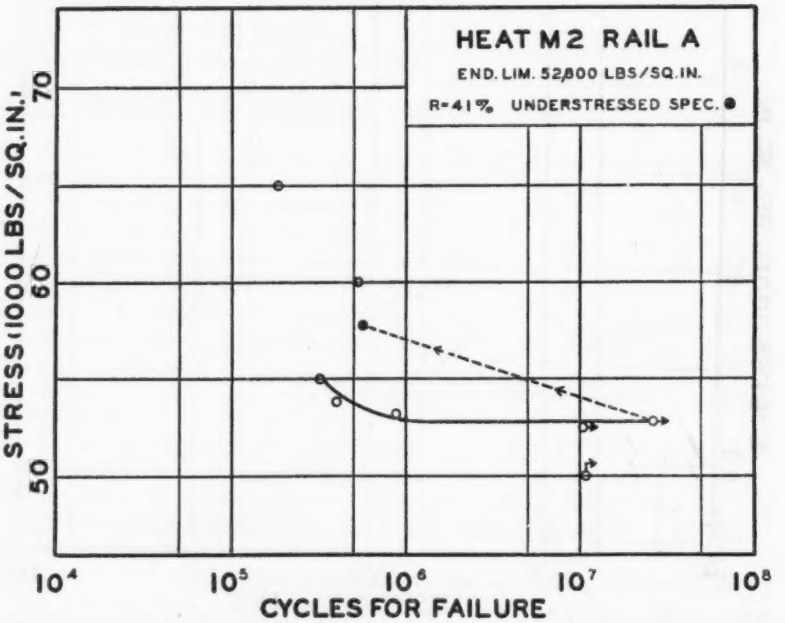

FIGURE 6.—*Endurance curve for medium manganese rail steel, A rail, heat M–2*

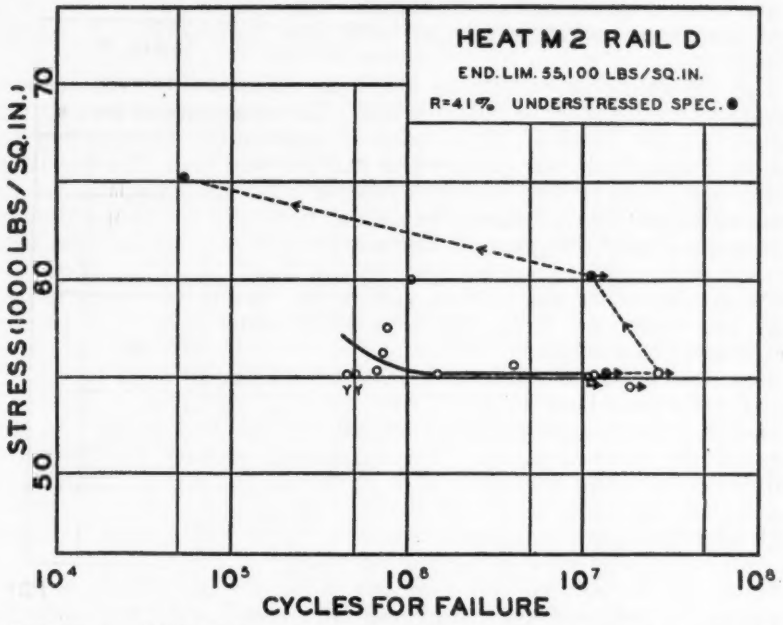

FIGURE 7.—*Endurance curve for medium manganese rail steel, D rail, heat M–2*

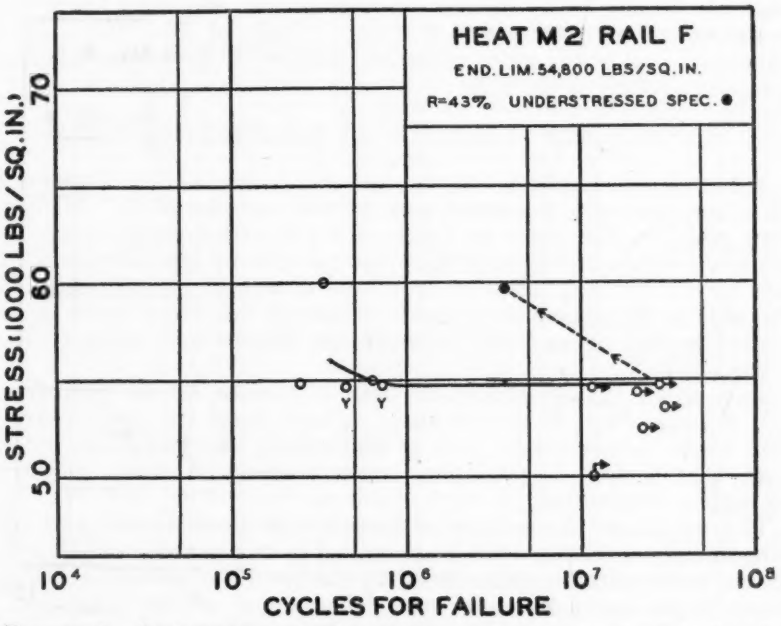

FIGURE 8.—*Endurance curve for medium manganese rail steel, F rail, heat M–2*

The results of the tests of specimens from the F rail of this same heat are given in Figure 5. An endurance limit of 67,000 lbs./in.^{2} is indicated.

The difference in endurance limits as indicated by the tests of specimens from the three rails is small. The average value is approximately 67,300 lbs./in.^{2} This value is appreciably higher than the values obtained on new or serviced carbon steel rails, the results of which are given in the previous reports with the exception of the value of 67,500 lbs./in.^{2} shown by similar tests of a transverse fissured carbon steel rail.[6] In general, the scatter of results of the data from the 1.5 per cent medium manganese rail (heat M–1) are about the same as shown by the carbon rail steels. As in the carbon steel rails the specimens from the Y position show somewhat inferior endurance properties.

The results of the endurance tests of specimens from the A, D, and F rails from heat M–2 (1.2 per cent Mn) are given in Figures 6, 7, and 8. Endurance limits of 52,800, 55,100, and 54,800 lbs./in.^{2}, respectively, were obtained. The agreement between the individual rails is good. The average value of 53,450 lbs./in.^{2} is appreciably lower than the value of 67,300 lbs./in.^{2} obtained for the steel (M–1) with slightly higher manganese content. It is well within the range of endurance properties of carbon rail steels.

It should be pointed out that the difference in endurance limits between the two medium manganese rail steels is not necessarily due to the slight difference in manganese contents and the slightly higher carbon content of the higher manganese steel. It is well known that increasing the manganese content in steels, especially with relatively high carbon content, increases the tendency toward air hardening. The difference in endurance limits of these two medium manganese rail steels may, therefore, be due in part to a difference in rate of cooling of the rails.

4. ENDURANCE PROPERTIES OF HEAT-TREATED RAILS

Although the hardness survey had not indicated any measurable differences between the outer and central portions of the rail heads from which a difference in endurance properties might have been predicted, it was recognized that the relation of hardness to endurance properties is qualitative only, and it was, therefore, considered desirable to determine experimentally if any difference in endurance properties was to be found between the central and outer portions of the head.

Two series of test specimens were therefore taken from the C rail of heats H–1, H–2, and H–3. These series of test specimens were taken contiguously (end to end) along the length of the rail from the U and Y positions, respectively, and their endurance properties determined.

The results of the endurance tests of the heat-treated and comparison rail steels may then be classified in two groups, one in which the endurance limit is determined by the results of tests of specimens taken in the usual manner across the section of the head (fig. 2) and the other as determined by specimens taken only from the U and Y positions, respectively.

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[6] Rail from heat P. O. See p. 241 of reference 2.

The results of the former are given in Figures 9 to 16, inclusive, and of the latter in Figures 17 to 19, inclusive.

The results of tests of specimens from the A, C, and F rails of heat H–1 (30 seconds quench) are given in Figures 9, 10, and 11. The indicated endurance limits are 77,000, 68,500, and 74,000 lbs./in.^{2}, respectively. The average value is approximately 73,170 lbs./in.^{2}.

The results of tests of specimens from the A, C, and F rails of heat H–2 (15 seconds quench) are given in Figures 12, 13, and 14, respectively. The indicated endurance limits are 80,000 and 76,000 lbs./in.^{2} for the A and C rails and greater than 67,000 lbs./in.^{2} for the F rail. In the tests of the specimens from the F rail an unusually marked scatter of results was apparent. One specimen ran 25,000,000 cycles at 75,000 lbs./in.^{2} without failure. All other specimens failed at stresses above approximately 67,000 lbs./in.^{2}. Of these there were four specimens including three from the Y position which showed appreciably inferior endurance properties. This marked scatter indicated a relatively marked inhomogeneity, the cause of which was not apparent.

The results of tests of the C and F rails of the comparison heat made under normal conditions are given in Figures 15 and 16. Endurance limits of 59,500 and 55,500 lbs./in.^{2}, respectively, were found which gives an average value of 57,500 lbs./in.^{2}.

It is evident from the above data that under the same conditions of sampling and testing, the endurance limit of the heat-treated rail steels is appreciably higher than the endurance limit of the untreated "normal practice" rail steel. The endurance properties of the heat-treated rail steels in both instances are also somewhat superior to the values indicated by the tests of the medium manganese rail steels containing 1.5 per cent manganese and are markedly superior to the 1.2 per cent medium manganese rail steels.

The results of tests to determine the relative endurance properties of steel from the central and outer portions of the head of the rail from the several heats are given in Figures 17 to 19, inclusive. It is evident in comparing the data in Figures 17 (*a*) and (*b*), for the C rail from heat H–1 (quenched 30 seconds) that there is a marked difference in the endurance properties indicated by the tests of specimens from the U and Y positions. (Fig. 2.) The former has an indicated endurance limit of 79,000 lbs./in.^{2} as compared to 65,000 lbs./in.^{2} for the latter, a difference of 14,000 lbs./in.^{2}.

Similarly, the results given in Figures 18 (*a*) and (*b*), of comparative tests made of specimens from the U and Y positions of the C rail from heat H–2 (quenched 15 seconds) show the marked difference of 21,800 lbs./in.^{2}, the specimens from the U position indicating an endurance limit of 85,200 lbs./in.^{2} as compared to 63,400 lbs./in.^{2} indicated by specimens from the Y position.

That these differences in endurance properties between the outer and central portions of the head of the rail are probably related to a mass effect in the heat treatment is borne out by the results of a similar comparison of the endurance properties of the outer (U) and central (Y) portions of the head of the C rail from heat H–3 which was not heat treated but made in accordance with normal practice. The results of these tests are given in Figures 19 (*a*) and (*b*). It is evident that the respective endurance limits of 59,000 and 59,400 lbs./in.^{2} are

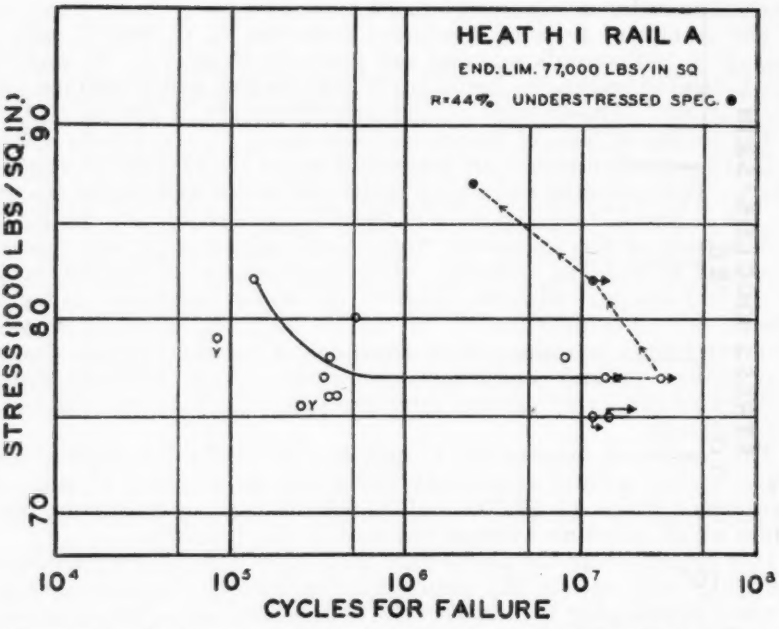


FIGURE 9.—*Endurance curve for heat-treated rail steel, A rail, heat H–1*

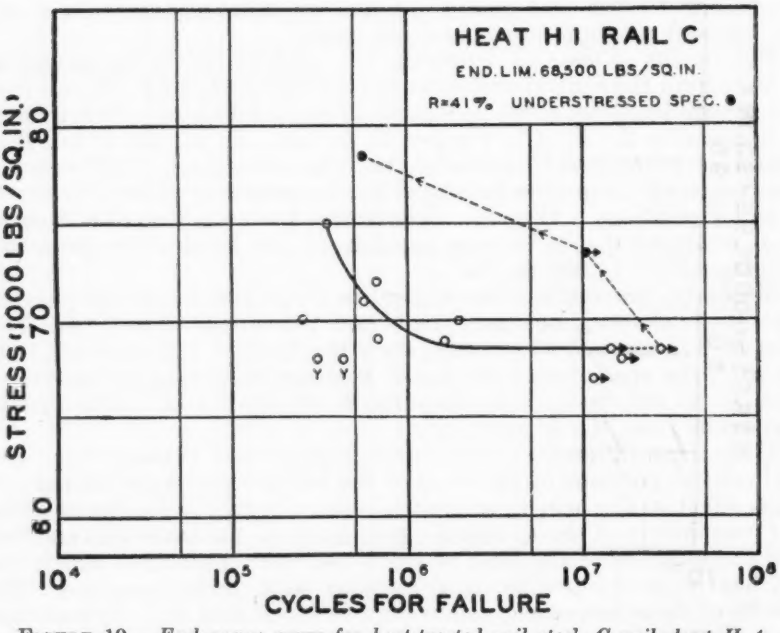


FIGURE 10.—*Endurance curve for heat-treated rail steel, C rail, heat H–1*

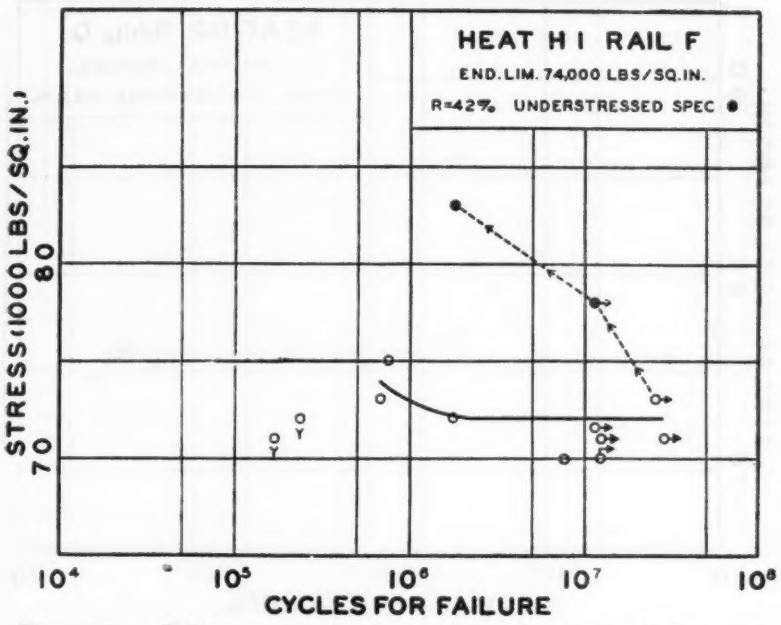


FIGURE 11.—*Endurance curve for heat-treated rail steel, F rail, heat H–1*

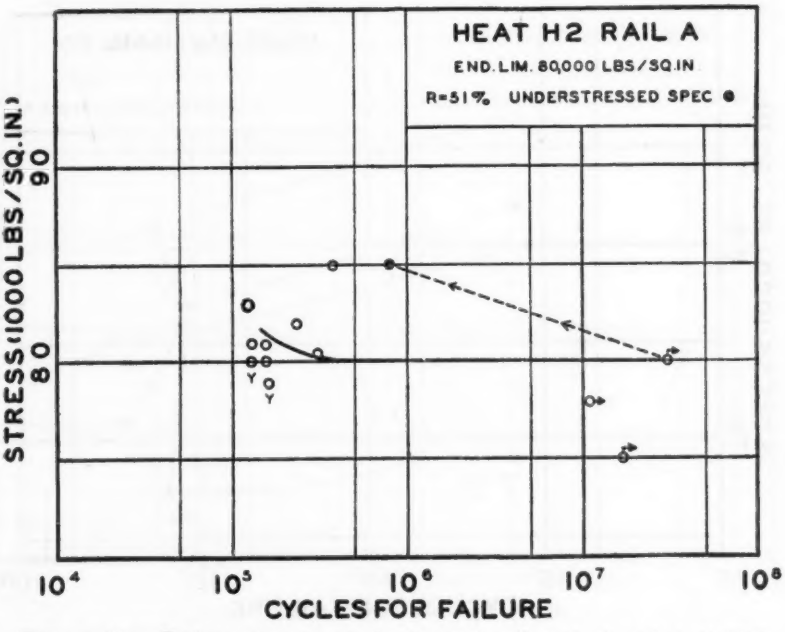


FIGURE 12.—*Endurance curve for heat-treated rail steel, A rail, heat H–2*

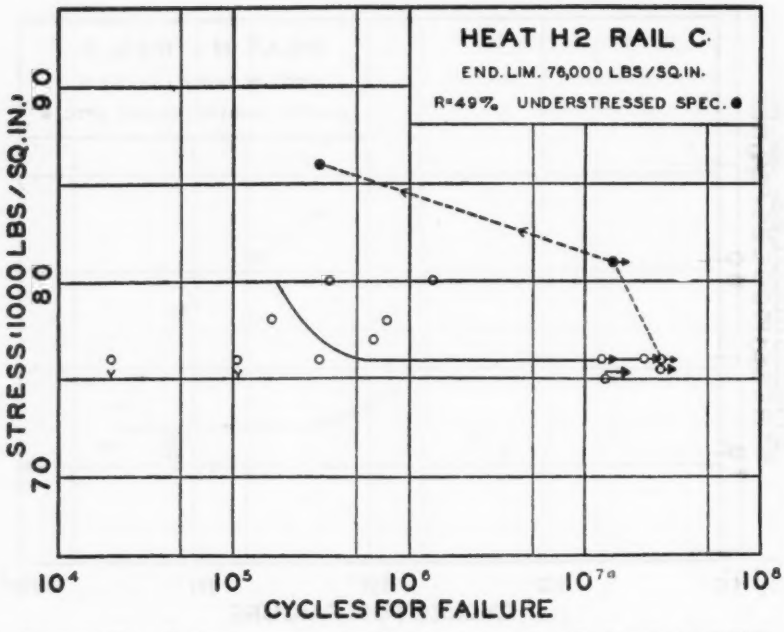


FIGURE 13.—*Endurance curve for heat-treated rail steel, C rail, heat H–2*

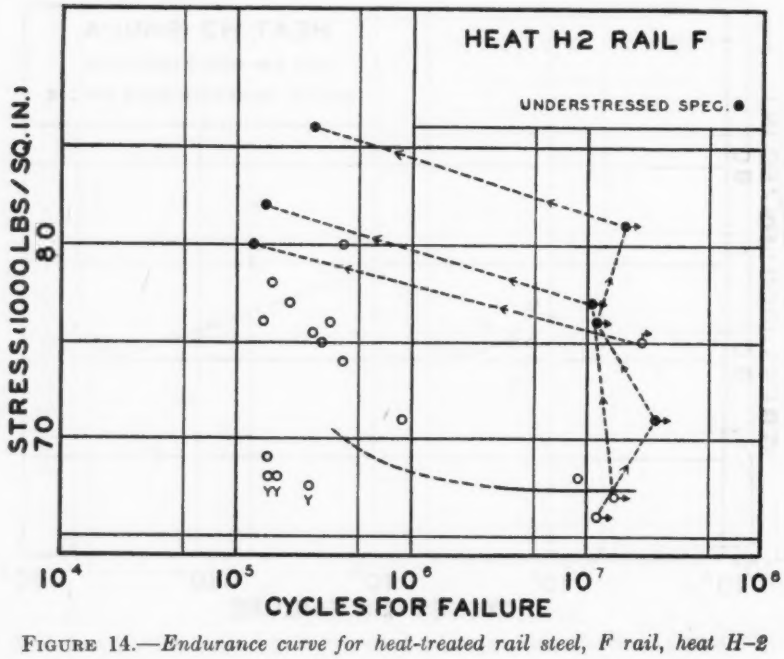


FIGURE 14.—*Endurance curve for heat-treated rail steel, F rail, heat H–2*

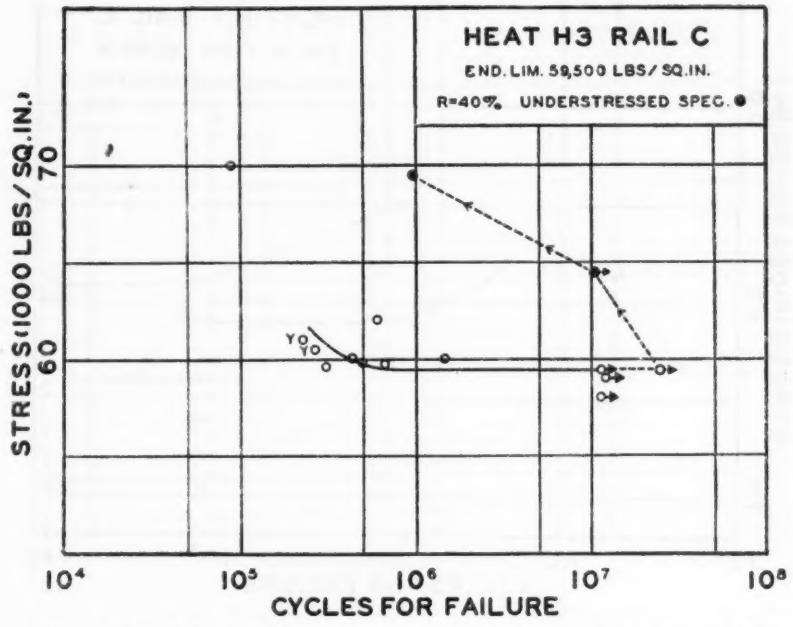


FIGURE 15.—*Endurance curve from "normal practice" rail, C rail, heat H–3*

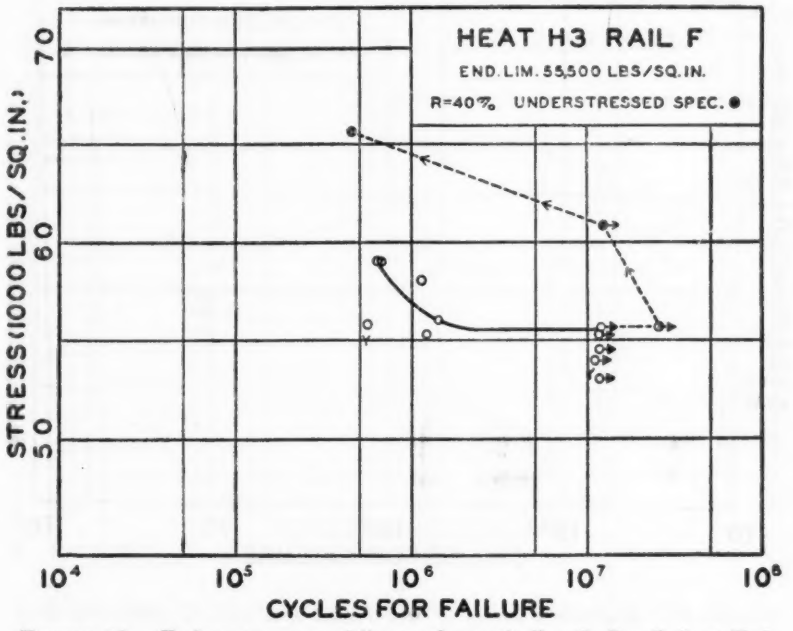
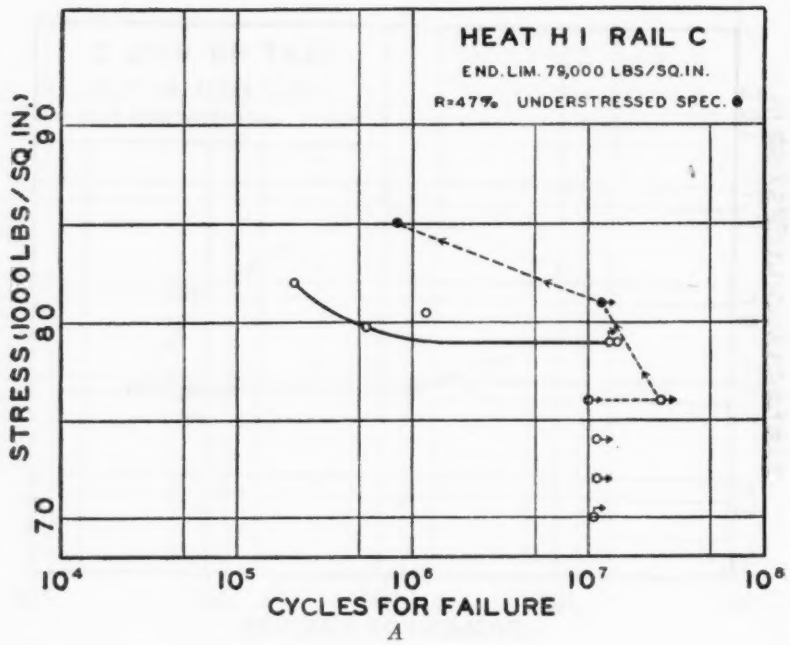
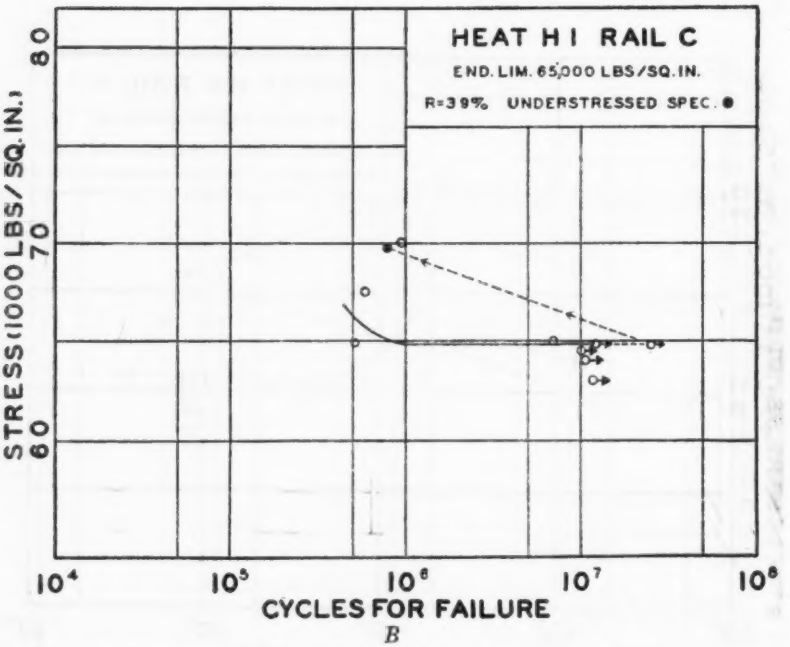


FIGURE 16.—*Endurance curve of "normal practice" rail, F rail, heat H–3*



A



B

FIGURE 17.—*Endurance curves of heat-treated rail steel, C rail, heat H–1*

A, all specimens taken contiguously from U position
B, all specimens taken contiguously from Y position

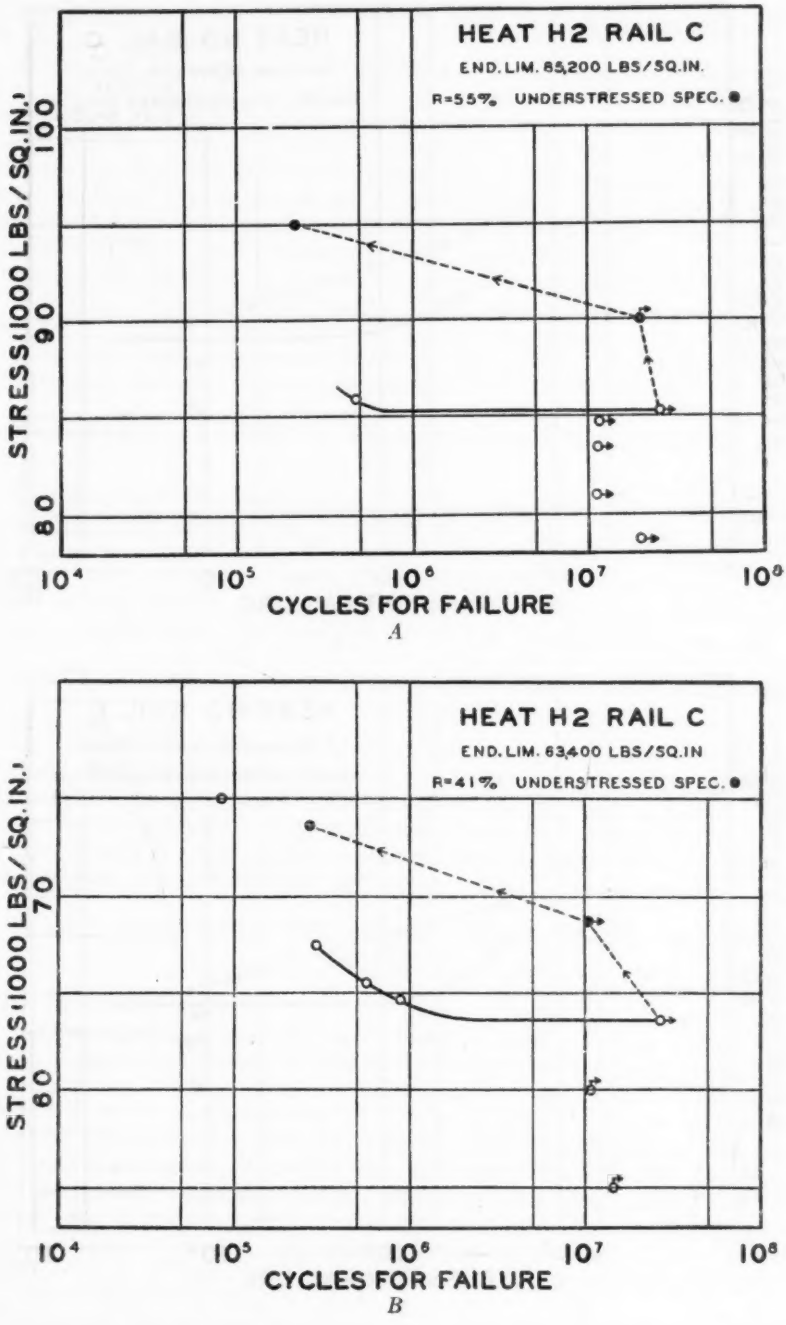
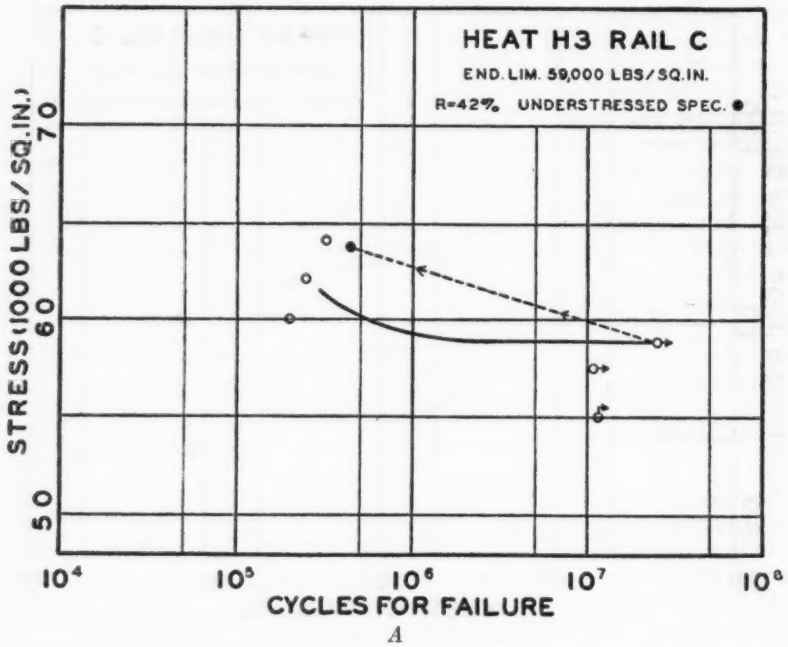
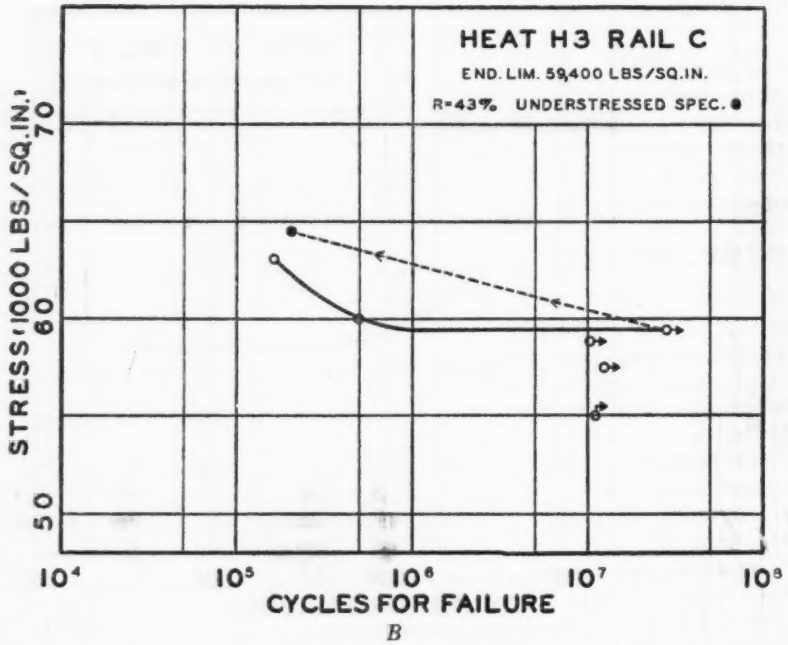


FIGURE 18.—*Endurance curves of heat-treated rail steel, C rail, heat H–2*

A, all specimens taken contiguously from the U position
B, all specimens taken contiguously from the Y position



A



B

FIGURE 19.—*Endurance curves of "normal practice" rail steel, C rail, heat H–3*

A, all specimens taken contiguously from the U position
B, all specimens taken contiguously from the Y position

practically identical. Similar results were obtained in tests reported in the previous work.[7]

In making a comparison of the effect of the differences in heat treatment of the rails on the relative endurance limits obtained it should be pointed out that unfortunately the rails representative of each condition were from different heats of steel. In the previous work it was shown that the endurance properties of rail steel may vary from heat to heat[8] by as much as 13,000 lbs./in.^{2}. It is, therefore, not possible to state definitely whether the differences noted between the 30-second (H–1) and 15-second (H–2) quenched rail are a result of the difference in heat treatment or an inherent difference in the heats.

Whether the lack of uniformity of endurance properties across the section of the quenched rails is disadvantageous or possibly advantageous can not be stated without a knowledge of the distribution of stress in the head of a rail in service.

5. ENDURANCE PROPERTIES OF MANGANESE MOLYBDENUM RAIL STEEL

The results of the endurance tests of specimens from the manganese molybdenum rail are given in Figure 20. The data indicate an endurance limit of 62,600 lbs./in.^{2}. The scatter was appreciable. Further tests should be made on steel from other rails from similar heats before definite conclusions are drawn. The value indicated is slightly higher than the average found for standard practice rail.

6. ENDURANCE PROPERTIES OF A MEDIUM MANGANESE RAIL STEEL TREATED WITH ZIRCONIUM

The results of endurance tests of specimens from the F rail of a medium manganese rail steel treated with zirconium are given in Figure 21. An endurance limit of 65,000 lbs./in.^{2} is indicated. The scatter is appreciable. The endurance limit is practically the same as was found for the medium manganese rail steel (M–1) of similar composition but not treated with zirconium.

V. SOME FURTHER TESTS OF TRANSVERSE FISSURED RAILS

In one of the previous reports[9] data are given on the endurance properties of steel from transverse fissured rails. It was shown that the endurance properties of the steel in the fissured rails was equal to or greater than in similar rail which had not failed after being subjected to the same amount of service in track. These tests were made on rails removed from track on the Pennsylvania and Canadian National Railroads. Through the courtesy of J. M. R. Fairbain, chief engineer, Canadian Pacific Railway, two more rails were obtained, one of which had failed in service from a transverse fissure and the other, although subjected to identical service, had not failed. The markings on both rails indicated they were from heat No. 8501–111–08 of Dominion Iron & Steel Co.

Endurance tests were made on specimens taken from the heads of each rail in the usual manner. (Fig. 2.) The results of these

[7] See p. 293, fig. 21 of reference 1. [8] See p. 292 of reference No. 1. [9] See p. 237, reference 2.

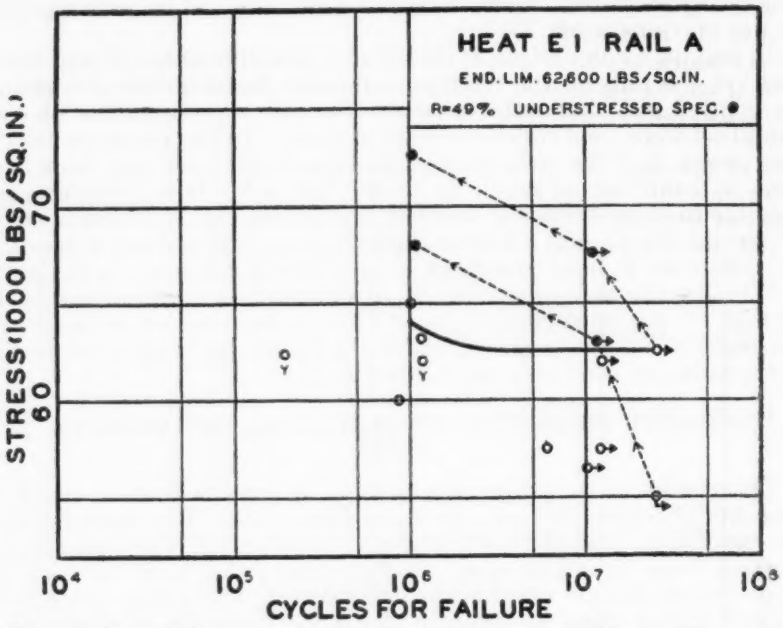


FIGURE 20.—*Endurance curve of a manganese molybdenum rail steel. A rail, heat E–1*

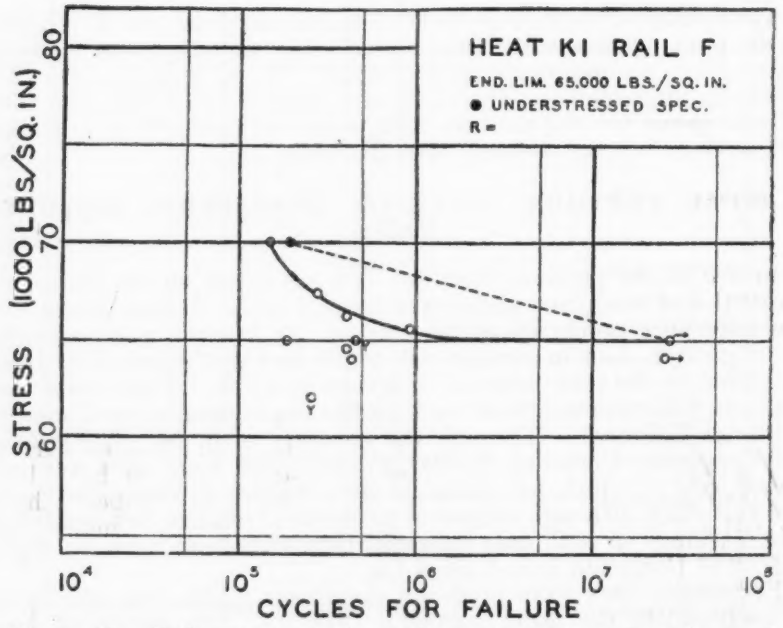


FIGURE 21.—*Endurance curve of a medium manganese rail steel treated with zirconium, F rail, heat K–1*

tests are given in Figure 22. The data indicate that the endurance limit of the steel from the fissured rail is slightly less than that from the unfissured rail. The "scatter" of results, shown by the specimens from the fissured rail is, however, quite marked. Deep etching of the test specimens showed this scatter to be due to the presence of shatter cracks in the steel, as was found in the previously reported tests of fissured rail. The specimens free from cracks indicated the endurance limit of sound portions of the steel to be well within the range of endurance limits that have been found in previous studies of rail steels that have not failed in service. These tests confirm

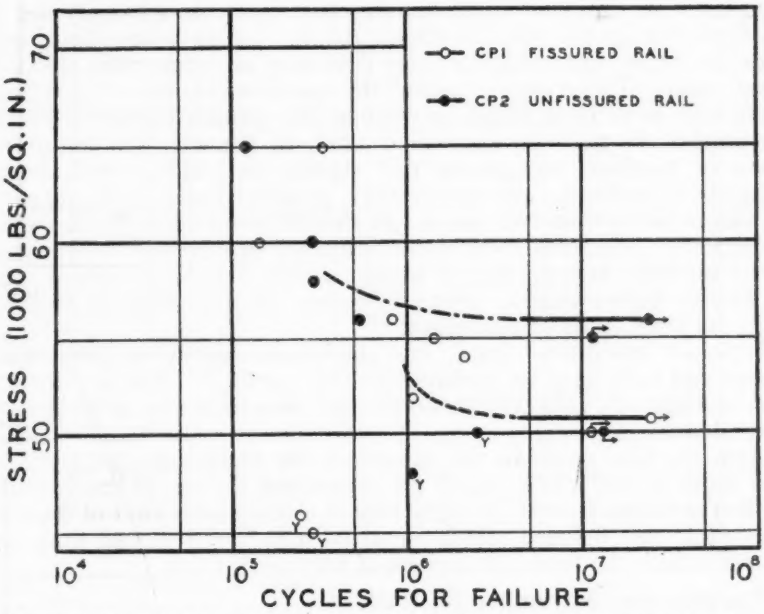


FIGURE 22.—*Endurance curves of steel from fissured rail (CP1) and unfissured rail (CP2) after same service*

the previous tests in showing that fatigue failure in rails (transverse fissures) probably starts from a nucleus such as a shatter crack or other similar internal defect.

VI. SUMMARY AND CONCLUSIONS

By request of the special joint subcommittee of the Rail Manufacturers Technical Committee and the Rail Committee of the American Railway Engineering Association a series of tests have been made to determine the endurance properties of some special heat-treated rail steels and medium manganese rail steels. Similar tests have also been made of a manganese molybdenum rail steel and a zirconium-treated medium manganese rail steel. Some further data are also given on tests of the endurance properties of steel from a transverse fissured and a comparison rail from the same heat which did not fail in service.

It has been found that the endurance properties of a rail steel may be appreciably increased by suitable heat treatment of the rail. Endurance limits of approximately 75,000 lbs./in.^{2} were obtained. It was also found that the endurance limit of the steel in the central portion of the head of a quenched rail may be appreciably less than in the outer portions of the head.

The endurance limit of a medium manganese rail steel containing 1.5 per cent manganese and 0.65 per cent carbon was found to be about 67,000 lbs./in.^{2}. Another heat containing 1.2 per cent manganese and 0.60 per cent carbon was found to have the somewhat lower endurance limit of about 55,000 lbs./in.^{2} Since the amount of manganese in this heat approximates the lower limit usually set for this type of steel the value of 55,000 lbs./in.^{2} for endurance limit indicates the lowest approximate value that may be expected in this type of rail steel. This value is within the maximum range of endurance limits that have been found to exist in the standard practice carbon rail steels. It may be concluded that, in general, the endurance limits of medium manganese rail steels, particularly with higher manganese contents, are appreciably greater than the corresponding values for carbon rail steels. It should be noted that the carbon content will also have appreciable influence on the endurance limits of the medium manganese rail steels, a higher carbon content tending to give higher values. Data, however, are not available to determine the magnitude of the effect.

Tests of specimens from one zirconium-treated medium manganese rail indicated an endurance limit of 65,000 lbs./in.^{2} for this type of steel. A value of 62,600 lbs./in.^{2} was found for a manganese molybdenum rail steel.

Data are also given in the report on the endurance properties of steel from a rail which failed by transverse fissure in track which confirm previous tests in showing that the endurance limit of the steel in a transverse fissured rail is equal to that found in rail that does not fail under the same conditions of service in track.

WASHINGTON, November 15, 1929.

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